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PHYSICAL CHEMISTRY

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The late Dr. H. P. Talbot was Consulting Editor of the
International Chemical Series from its inception in 1911 until
his death in 1927.

PHYSICAL CHEMISTRY

*An Elementary Text, Primarily for Biological and
Pre-medical Students*

BY

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PREFACE

This book has been developed from lecture notes used in a course intended primarily for biological students and given by the author at the Massachusetts Institute of Technology for the past seven years. To these notes has been added Chapter XXVI, which was prepared at the suggestion of Dr. Kenneth C. Blanchard.

Certain subjects that are often included in physical chemistry but are not taken up here are modern atomic theory, crystal structure, and photochemistry. There is no chapter on colloid chemistry, but it is believed that most of the important physical chemistry of colloids is presented, the principal omissions being of a descriptive nature. The subject matter has been thus limited in order to make possible a high degree of unity.

No attempt has been made to present experimental data for their own sake, nor for the purpose of examining the degree of accuracy of the laws of physical chemistry. The compilation of "International Critical Tables"¹ is now the great source of information as regards the experimental data of physical chemistry, for all who do not wish to collate and examine critically for themselves the data of many observers.

A knowledge of the rudiments of algebra is presupposed, as well as some practice in reading algebraic equations or the willingness to acquire such practice. A few topics require a knowledge of the notation of calculus; this may readily be gained by any determined student who happens not to have studied the subject. A previous study of calculus, and also of physics, is however of great advantage; not so much, in the opinion of the author, on account of the information gained in these studies and used without explanation in this book, as because of the experience gained in solving mathematical problems and in thinking about physical phenomena. This experience seems to give a power, definitely transferable to another scientific study.

¹ McGraw-Hill Book Company, Inc., New York, 7 volumes and paper-covered index, 1926-1930. There is also a good index at the end of Vol. 5.

Physical chemistry may be taught to students of chemistry with little or no reference to thermodynamics, as they may be expected to take advanced courses. But no suitable advanced courses are ordinarily available to biological students, and the necessary elementary acquaintance with thermodynamics must be imparted in their course in physical chemistry.

A large proportion of biological students go into research work, and this fact has been kept in mind. An attempt has been made to prepare the reader intelligently to consult standard authorities, to bridge the gap between the teaching of elementary principles and the thought and practice of specialists, and, in general, to give him such aid of this sort as is possible without interfering with the presentation of general principles. The book may therefore be useful to biologists, trained in an earlier school of physical chemistry, who now, being engaged in research, wish to increase their power.

Thanks are due in particular to Professors James A. Beattie and George Scatchard, who read the manuscript and made suggestions greatly appreciated.

LOUIS J. GILLESPIE.

CAMBRIDGE, MASS.,
August, 1931.

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PHYSICAL CHEMISTRY

CHAPTER I

INTRODUCTION. THE PHASE RULE

Physical chemistry partakes of both physics and chemistry, as the name implies. Its definition is somewhat elastic and depends partly on what is taught in college courses, partly on the content of books bearing the title, and considerably on the attitude and reactions of men who are called physical chemists. Indeed, physical chemistry has been amusingly called a state of mind, and it is probable that the student will find some truth in this remark.

The subject is certainly characterized by its interests. These lie principally in the generalizations which can be made of the physical behavior of chemical substances or combinations of them. The physical chemist has been able to extend the meaning of physical behavior; he can treat the decomposition of chalk into carbon dioxide and lime as a physical process. He has also found generalizations concerning the velocity of chemical reactions which depend on the chemistry of the reaction only in a minor way.

Many of the generalizations can be used without a detailed knowledge of the chemical composition of the substance under consideration. It is exactly in biology that such generalizations are of great value, since we are here usually forced to deal with substances concerning whose composition we know little or nothing. A noteworthy example is the definition and actual measurement of acidity in fluids of unknown composition by the so-called hydrogen-electrode or indicator methods.

Although some of the topics treated here may appear disconnected, the student will find it an easy matter to maintain perspective if he will remember that the purpose of this book is

primarily to treat of chemical equilibrium, first and mainly of the conditions of equilibrium and finally of the velocity with which equilibrium is reached in chemical systems.

One of the broadest generalizations of physical chemistry is the so-called phase rule of J. Willard Gibbs. We begin with a brief introduction to the meaning of this rule or law.

1. The State of a Phase.—If we try to mix oil and water by shaking them together we find that they ultimately separate, on standing, into two distinct homogeneous parts, an oily layer and a watery layer. Such a homogeneous part of a system is called a phase, whether it is gaseous, liquid, or solid, and whether it is a pure substance or a solution. A phase may be subdivided; a precipitate, such as that obtained by adding hydrochloric acid to a solution of silver nitrate, may usually be regarded as one solid phase if it is a pure substance.

We shall regard the condition or *state* of a phase as being fully described when its density, temperature and composition, and the pressure upon it are given. The composition can be stated by naming the components of the system and giving their percentages so that one would be able to make up a gram of the phase. If there is only one component the percentage is necessarily 100 and need not be stated; if there are two components only one percentage needs statement; and the student will perceive that if there are c components we shall need to state $c - 1$ percentages. To complete a description of the state of the phase we shall need to give also the pressure, the density, and the temperature. This makes a total of $c + 2$ quantities which must be given in order fully to describe the state of a phase.

This number of quantities will suffice, and the phase rule will hold, only when the substances under consideration are not being appreciably influenced by gravity, electricity or magnetism, light, surface tension, or distortion (of solids).

2. The Phase Rule.—Experience shows that the state of a phase will be fixed, that is, fully determined, when we fix the values of all but one of the above $c + 2$ quantities; the value of the remaining one then being fixed by nature. For example, if we take pure water, fix its pressure at 1 atm. and its temperature at 20° , its density will be fixed by nature and we can measure it. If we do not fix the pressure and especially the temperature,

the density will vary irregularly and we cannot measure it satisfactorily. In the case of a solution such as urine, the density will not be fixed even when both pressure and temperature are fixed, but will vary with different samples, according to the composition.

When the system under consideration comprises more than one phase, all phases being at the same temperature and pressure, still fewer quantities need to be fixed by us in order that nature will fix the rest of the $c + 2$ quantities, and, indeed, *one less quantity for each extra phase*. According to the phase rule we can find the number V of variables which we must fix to determine (with the aid of nature) the state of all the phases of the system by subtracting from $c + 2$ the number p of phases into which the system is divided at equilibrium. By equilibrium we mean here a condition in which there is no tendency for phases to disappear, for substances to pass from one phase to another, or for any chemical reactions which have been taking place to proceed further. The number V is called the variance of the system. The phase rule is then given by the simple equation

$$V = c + 2 - p. \quad (1)$$

It is usually easy, though not always, to count correctly the number of components when we know the composition. If no chemical or ionic reactions take place, the number of components is simply the number of different substances present in the system. They need not all be present in every phase, but if a liquid solution is present it is safe to assume that all components are present in it. In general, c means the number of *independently variable* components, and if chemical reactions take place we count the total number of different substances present, including those substances that may be formed by the chemical reactions, and subtract the number of restrictions that are placed on the concentrations of the substances, each independent chemical reaction that can take place being counted as one restriction.¹

In general the number of components cannot be predicted without a knowledge of the chemical reactions that will occur under the conditions of the experimentation.

Ions, though they are not really substances, but essentially parts of substances incapable of independent existence in ordinary chemical experimentation, may be considered as components if we remember the restriction

¹ If the reaction goes to completion (or fails to proceed at all) there is obviously one restriction. If it goes until equilibrium is reached, there will be a mass action equation of some form or other which will exactly express the restriction.

due to the fact that the interior of a phase must be electrically neutral; that is, there must be as many positively charged ions as negatively charged ions.

It is not easy to give a brief and entirely satisfactory rule by which the number of components can easily be computed in every case; and this will not be attempted here, as in our application of the phase rule it will always be a simple matter to count the components.

It may happen that a phase is also a pure substance, either one of the components, or a substance produced from them by a chemical reaction. In such a case there may be more than one choice of substances that can be called the components, but the number of components will always be the same.

Suppose now we fix a number of variables equal to V . Nature will fix the values of the other variables but may not do this instantaneously. Thus, if we bring salt into contact with water at 1 atm. and 20° *, keeping an excess of salt present, we have two phases, solid salt and solution, and two components, so that $V = 2 + 2 - 2$, corresponding to the fixing of the temperature and the pressure. Nature will now fix the percentage of salt in the solution, but experience shows that nature is slow. We must shake the two phases together for some time to fix the concentration of salt. When we think that it is fixed we may measure it. As a guarantee that we have reached the correct or equilibrium concentration we may increase the strength of the solution by shaking again at a higher temperature and then approach the equilibrium concentration by restoring the temperature to 20° and shaking again. Such a procedure is known as approaching the equilibrium from both sides. The equilibrium concentration is known as the solubility of the particular solid phase in question. Some salts exhibit different solid phases, which are generally stable in different temperature ranges.

In the above case there would normally be air present in contact with the salt and solution, and this would mean another phase and more components. But the effect of dissolved air is so slight that the results would be the same if the air were replaced by a solid plunger exerting the same pressure. Hence we get the correct phase rule count most simply by considering the air as a mere mechanical plunger and counting the air neither as a phase nor as a component.

* When not otherwise stated, temperatures given numerically will always be the ordinary Centigrade temperature.

Not all systems are in equilibrium for which the variance V is exactly equal to the number of variables fixed by us. Thus, at 0°C . and 1 atm., solid salt and ice might be in equilibrium so far as the phase rule is concerned. But if a little liquid water should be present, perhaps on the surface of the ice, we should have $V = 1$, and since two variables have been fixed we have overspecified our system. What happens here is that the ice begins to melt and the salt to dissolve. If we maintain the temperature at 0° the melting and solution keep up until either the ice or the salt is gone. The variance is then 2 and the system is stable.

In general, overspecified systems are not in equilibrium. When we wish to make sure that the phases present are the right ones for a stable system we may always apply the test of adding a little of some phase that might reasonably be expected to be a part of the equilibrium system, and observe whether this phase disappears or is formed at the expense of any of the phases originally present.

3. The Volume of a Phase.—The density is the quantity of substance per unit volume, usually given in grams per cubic centimeter. It is sometimes given in grams per milliliter. This is really specific gravity, since the milliliter is the volume of one gram of water at 1 atm. and at its temperature of maximum density (about 4°C .). Since one milliliter is equivalent to 1.000027 cc., the distinction between the two is important only in the most refined measurements.

The ratio of mass to volume is therefore fixed when the temperature, pressure, and composition are fixed, and it follows that x grams of substance occupy exactly x times the volume of one gram when the temperature, pressure, and composition are the same for both quantities.¹ This principle is used in the laboratory measurement of volume. A similar principle does not hold for temperature, nor, except in the case of "ideal" gases, for the pressure.

4. Equilibrium in General.—Equilibrium may be defined as a state or condition independent of the time. This implies that

¹ This being a consequence of the phase rule, it implies that gravity is of no appreciable influence. In the case of a long vertical column of a heavy liquid, we might have to distinguish different pressures at different levels.

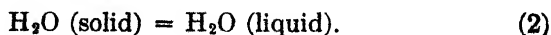
nothing is happening to change the state. We do not imply that molecules cease to move; on the contrary, they may move about from one phase to another, or even react together chemically, and we shall still have equilibrium provided that the net amount of each phase and of each substance in the system is constant. For the state of a system does not refer directly to the position or velocity of individual molecules, but to the values of the density, temperature, pressure, etc., all of which are statistical quantities referring to the average tangible effects of enormous numbers of molecules.

The above definition is not perfectly satisfactory from a practical point of view. For there never occurs in nature, nor is achieved in the laboratory, a state or condition independent of the time. Everything changes. Suppose we wish to study a system which includes water. If we use a container of glass, the glass will slowly dissolve; if we use steel, it may react with the water. Even with an ideal container there is a possibility that the water will partially decompose into hydrogen and oxygen gases.

We might escape the difficulty by talking about an equilibrium as it might be realized under ideal circumstances, with an ideally insoluble and inert container, and even with some ideal water which is imagined totally incapable of decomposition. It seems better to avoid any necessity for such a stretch of the imagination.

The difficulty with the above definition of equilibrium lies in its absolute character. All equilibria studied in the laboratory are relative. They are relative to some particular change or changes of state. (Equilibrium may be defined with reference to some particular kind of change as the condition in which there is no tendency for this kind of change to take place.) This means of course no net tendency: there may be an active tendency to produce the change in one direction provided it is exactly balanced by an active tendency in the opposite direction, and in fact this is the only kind of equilibrium that can be satisfactorily studied by experiment.

We may for instance consider the equilibrium between ice and water. We may describe the kind of change to which equilibrium relates by a simple equation:



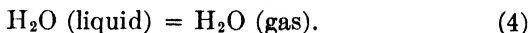
At the temperatures at which ordinary ice is stable the reaction



will not trouble us. We say that equilibrium with reference to reaction (3), or, more briefly, that the equilibrium (3) is not realized.

In accordance with sound theory it is customary to speak of different equilibria as quite distinct matters, even though they involve the same substances.

It is of course possible sometimes to have more than one equilibrium realized in the same system, for instance the equilibrium (2), and the equilibrium



Thermodynamics gives us some important mathematical equations relating to equilibrium. Because of the growing significance of thermodynamics to the student of biology or chemistry it is important for him to know that for the use of these equations a knowledge of absolute equilibrium is never required, as the equations may all be applied to data obtained for equilibrium with reference to definite and particular changes.

The words *dynamic equilibrium* are often used with reference to an equilibrium such as (3) to emphasize our belief that in the equilibrium state, which can be realized at high temperatures especially with the aid of a catalyst, water molecules are continually decomposing, but are being continually formed at an equal rate by combination of the elements. A similar viewpoint is taken towards other equilibria, such as (2) and (4).

Problems

1. (a) What is the largest number of phases which can exist together in equilibrium in a system composed of sodium chloride and water if we keep the pressure constant at 1 atm. and the temperature constant at 0° ? (b) If we merely keep the pressure constant at 1 atm. and let nature take care of the temperature? (c) If we do not ourselves fix any variables?

2. Using if necessary a handbook containing physical constants of chemical substances, find (a) several examples of elements which can appear when pure in more than one solid phase and find (b) some examples of sodium salts which, in systems containing water as a component, may give rise to more than one solid phase containing the saline component.

3. Considering definiteness of state and equilibrium, answer the following very briefly: What is generally true of underspecified systems; of exactly specified systems; of overspecified systems?

4. Use the phase rule to explain why it is advisable to read the barometer when determining the boiling point of a pure liquid. The boiling point is the temperature at which the liquid and its vapor are in equilibrium. Improve this definition.

CHAPTER II

A SIMPLE THEORY OF GASES

If we take a pure substance in the gaseous state, or a definite gaseous mixture such as air, we can measure its pressure if we fix its density and temperature. The density will be fixed by putting a definite mass of gas into a definite volume; the temperature, by immersing the container in a constant temperature bath. The pressure is commonly measured by observing in a manometer tube the height of a column of pure mercury which the pressure can support in an upright tube; the temperature of the column is noted, and by calculation the height of a column of pure mercury at 0°C. which the pressure would support is found. If the column is contained in a narrow tube, the correction for capillarity may be important. This correction depends not only on the radius of the tube, but also on the height of the meniscus. In precise work, account is taken of the value of the acceleration of gravity at the laboratory, as this affects the weight of a column of mercury.

Many experiments have been made to find exactly how the pressure depends on the density and temperature. These show that this dependence is not the same for different gases, unless the density (and therefore also the pressure) is low.

At low pressures, however, such as those existing in and around the animal body, the dependence is practically the same for all gases and is expressed by the simple laws of Boyle, of Avogadro, and of Gay-Lussac.

5. Boyle's Law.—If the temperature of a definite mass of gas is held constant, the density is directly proportional to the pressure.

6. Avogadro's Law.—At the same temperature and pressure, equal volumes of different gases contain equal numbers of molecules and therefore of gram molecules; that is, different gases at the same temperature and pressure have the same molal density—

the molal density being the number of gram molecules, or simply moles, per unit volume.

Let us express these laws in symbols, using p for pressure, d for molal density, t for temperature, V for volume, and n for the number of moles present in the volume. Boyle's law is then

$$p \propto d \quad (1)$$

at constant temperature, or

$$p = k_1 d = k_1 n/V, \quad (1a)$$

where k_1 is a number dependent on the temperature for its value, but constant when the temperature is constant. Avogadro's law is now simply: k_1 is the same for different gases.

In the laboratory we weigh material in grams, not in moles.¹ The number of moles in a given number of grams, m (for mass), is found by dividing this number by the molecular weight M :

$$n = m/M. \quad (2)$$

The molecular weight is equal to the atomic weight or a simple multiple of it (usually two), as expressed by the customary formula, such as He, H₂, N₂, etc.

The molecular weight is calculated from the results of chemical analysis when analysis of compounds is possible. But, as we know, chemical analysis does not decide between a correct molecular weight and a multiple of it, when we do not know the formula. Hence the above laws are used in selecting the correct value. For the inert gases, He, Ne, Ar, Kr, and Xe, which do not form compounds and have therefore but one atom per molecule, the above laws are used to calculate the molecular weights. In this case we have to take into account the approximate character of these laws and find improvements of them because a high precision is needed.

Other methods have also been used in the development of our system of atomic and molecular weights, which are important in the history of chemistry, but are not discussed here.

7. Gay-Lussac's Law.—This states that the volume of a given mass of gas, kept always at the same pressure, varies linearly with the temperature. If we plot the volume against the temperature t in Centigrade degrees as read on a mercury thermom-

¹ That is, we determine the mass by comparing on a balance its weight with the weight of standards of mass.

eter we obtain a picture like that in Fig. 1, provided the gas remains a gas and does not condense at the lower temperatures. The variation is said to be linear because the points lie nearly or quite on a straight line. When this line is continued to the left, as shown by the broken line, it intercepts the horizontal axis at about -273°C. , as shown. The equation of this line is

$$V = k_2(t + 273). \quad (3)$$

From Avogadro's law this constant k_2 , which depends on the number of moles and the pressure, is the same for different gases, as otherwise the volume of two gases containing the same number of moles at the same pressure might be indeed the same at one temperature, but not the same at other temperatures. We call the sum $(t + 273)$ the absolute temperature, and denote it by a

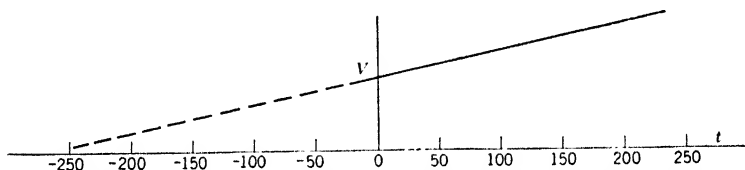


FIG. 1.—The volume V of a constant quantity of gas at constant pressure, at various values of the Centigrade temperature t .

capital T . A more precise value of the number to be used in changing from Centigrade to absolute is 273.13.

8. The Ideal Gas Law.—Equations (1) and (3) hold under different circumstances, Eq. (1) for constant temperature and Eq. (3) for constant pressure, so they may not be treated mathematically as simultaneous equations. The following equation, which may be derived from Eqs. (1a) and (3) by the use of an algebraic theorem on variation, will be seen to combine all their information:

$$pV = nRT, \quad (4)$$

where R is the same for all gases, n being the number of moles in the volume V . Thus from Eq. (4) we see that

$$V = (nR/p) \times T,$$

so that the volume is proportional to the absolute temperature when n and p are constant. It is left as a problem to show that

Eq. (4), which we shall call the ideal gas law, or ideal gas equation, contains the laws of Boyle and of Avogadro, as well as a modified form of the law of Gay-Lussac.

The value of the gas constant R depends on the units used in expressing the magnitudes of the various quantities involved in the equation in which it occurs. With regard to Eq. (4) various units may be used in expressing the magnitudes of the pressure, the volume, the temperature, and even the quantity of substance in the gas. For instance, engineers sometimes use pound moles instead of gram moles; physicists often use grams instead of moles, in which case the constant varies with the kind of gas. The temperature may be Fahrenheit absolute (degrees F. + 459.63), the pressure in pounds per square inch, etc. Although we shall adhere to units generally used by chemists so far as possible, the idea should be appreciated that one set of units is in no way more correct than another, so long as the units used in an equation are consistent.

It is now the usual practice to omit from general equations any symbols for conversion factors, which would correct the equation for the use, say, of atmospheres in one term of the equation and millimeters of mercury in another. One therefore makes sure to use consistent units, and when a *dimensional constant* such as R occurs, so-called because its value depends on its units or "dimensions," one finds the value of the constant corresponding to one's choice of units.

A convenient value of R is 0.08206, which is correct when the pressure is given in "normal" atmospheres, the volume in liters, the temperature in degrees Centigrade absolute, and the quantity of substance in (gram) moles. All this qualification is best expressed as follows:

The gas constant is 0.08206 $\frac{\text{liter-atm.}}{\text{degree C.-mole}}$. This gives not only the units for which the number is correct, but also the way in which they occur. We say that we have stated the dimensions of the constant, thus extending somewhat, though in a natural manner, the idea of dimensions as taught in elementary texts.

Compare Eq. (4) in the form $R = \frac{Vp}{Tn}$. There is now a proposition that is true of every good equation: every term in it

must contain the same units in the same way, *i. e.*, must have the same dimensions.¹ Hence the units of R must be those of the fraction $\frac{Vp}{Tn}$, and this is why we placed liters and atmospheres in the numerator of the expression following the number 0.08206, and degrees and moles in the denominator. The hyphens are used to indicate multiplication, as in *foot-pounds*, and the line for division. In speaking, the hyphen is omitted, and the word *per* used to represent division. We say "liter atmospheres per degree Centigrade and per mole," inserting the word *and* so as not to imply a double division (of degree by mole).²

There are several slightly different atmosphere units in use. A normal atmosphere is the pressure at the bottom of a wide tube of mercury at 0°C., the column of mercury being 760 mm. high, the density of the mercury being taken as exactly 13.5951 grams per cubic centimeter, and the column being subject to the standard gravity, $g = 980.665$. When experimental precision does not reach about one part in a thousand, one normal atmosphere may be regarded as the equivalent of 760 mm. of pure mercury at 0°C. in a wide tube at any laboratory. "International Critical Tables," McGraw-Hill Book Company, Inc., New York, contains in Vol. 1 information as to the value of g (pp. 396-400 and 402), and the corrections to be applied to barometers and manometers for temperature and capillarity (pp. 68-70).

9. Change of Units.—The dimensional constant R consists of two parts, the numerical value and the symbols representing the units in which the quantity is expressed. Nearly all the quantities met in physics have this character, including measured quantities, like 10 cc., and also conversion factors, such as 1,000 cc./liter. It is preferable to think *there are* 1,000 cc. *per liter* and write it as above, rather than to think 1,000 cc. *equals one liter*. By thinking and writing in the recommended way all physical quantities, whether measured quantities, conversion factors, or dimensional constants, may be treated alike; we may multiply or divide them in various ways, operating always both on the numbers and on their symbols in the same manner, and the results will all be correct, though only some may be useful. Thus if we divide

0.08206 $\frac{\text{liter-atm.}}{\text{degree C.-mole}}$ by 1,000 $\frac{\text{cc.}}{\text{liter}}$, we get 0.00008206

¹ If the equation contains logarithmic terms, this must be true of the equation at least after the logarithmic terms have been combined.

² This will be unnecessary if we ever come to speak of a degree-mole.

$\frac{(\text{liter})^2\text{-atm.}}{\text{cc.-mole-degree C.}}$, which is nothing we can use, though not incorrect, but if we multiply them together we observe that the liter is canceled, and we get a conversion factor often given, namely, $82.06 \frac{\text{cc.-atm.}}{\text{degree C.-mole}}$.

By the use of this system complicated changes of units can be carried out with great economy of thought.¹

10. Kinetic Interpretation of the Ideal Gas Law.—The simple behavior of gases at low pressures, together with other facts, notably those regarding the diffusion of gases, has led to the idea that a gas at low densities may be pictured as consisting of a large number of isolated molecules moving about rapidly and bouncing against the walls of the container of the gas, thus exerting a pressure against it. The gas does not lose its motion through frictional conversion to heat since heat itself is supposed due to the motion of the molecules.

This idea explains the fact that the pressure is proportional to the density. When worked out, it results in the equation

$$pV = \frac{1}{3}Nmc^2, \quad (5)$$

where N is the number of actual molecules in the volume V , m is the mass of each, and c is the mean velocity of the molecules. Comparison of Eq. (5) with $pV = RnT$ gives

$$\frac{2}{3}N\frac{mc^2}{2} = RnT. \quad (6)$$

Now physics teaches that the mean kinetic energy of a molecule, $mc^2/2$, is the same for different gases at the same temperature, at least when they are in the state in which the simple theory applies. From Eq. (6) this is therefore in accord with the convention that the number of molecules in a gram molecule, N/n , is the same for different gases. This number is called Avogadro's

¹ Some students may remember having been taught that it is not permissible to speak of division of one concrete number by another. Let them not be disturbed. It is permissible in natural science, and if "permitted" in arithmetic it would greatly facilitate the solution of many arithmetical problems, as the usefulness of the above system is by no means confined to changing units.

number and is 6.06×10^{23} molecules per mole, or atoms per gram atom, which nearly equals 6 followed by 23 cyphers. From Eq. (6) it follows that the absolute temperature is proportional to the mean kinetic energy.

Since $mc^2/2$ is the same for different gases at the same temperature, c^2 is inversely proportional to the mass m of a single molecule and therefore also to the molecular weight ($= 6.06 \times 10^{23} m$). In accordance with this the velocity with which a gas at a given temperature diffuses through a small hole has been found inversely proportional to the square root of its molecular weight. Diffusion through membranes does not always follow this rule, thus carbon dioxide passes through rubber membranes faster than some lighter gases.

Kinetic theory predicts that the viscosity of a gas, since this is proportional to the transfer of momentum to the walls of the tube through which the gas flows, will be greater at higher temperatures than at low. This behavior, the reverse of that shown by liquids, is in fact observed of gases, though the actual variation is not explained quantitatively by the theory.

11. Temperature.—In the above discussion temperature was not exactly defined, but was doubtless understood to be the temperature measured on a mercury thermometer. The physical chemist understands by absolute temperature the absolute temperature measured by means of a gas thermometer, and subjected to certain small corrections because the simple theory of gases does not express the behavior of any gas with perfect accuracy. A gas thermometer consists of a vessel containing a definite mass of gas, with conveniences for measuring either the pressure or the volume, while keeping the other quantity constant. If we keep the pressure constant and measure the volume, the arrangement is called a constant-pressure gas thermometer. With such a thermometer we may start from the beginning and measure temperature. First we may construct a diagram such as Fig. 1. For this we may define the temperature of melting ice (in equilibrium with water at 1 atm.) as 0°C. , and that of condensing steam at 1 atm. (in equilibrium with water) as 100° . We may measure the volumes of the gas at these two temperatures and plot them against 0 and 100 and draw a straight line through the two points. The intersection of this

line with the horizontal axis would give us the number 273, and we can now measure other temperatures by measuring volumes and using the line to find the temperature corresponding to any volume.

The determination of the corrections to be applied to such a thermometer has to be left to specialists. There are various methods, but it will suffice us to understand one.

The ideal gas equation holds so well at low pressures, that we believe in the kinetic picture as accurate for the conditions which it postulates. Of chief importance is the condition that the molecules be far enough apart so they do not influence one another in any way. This condition we know to be violated by gases at ordinary pressures. We suppose that the ideal gas equation may be applied to any gas for the purpose of calculating the pressure, the volume or the temperature, with great accuracy, if the pressure is low enough.

Making this supposition we may find the intersection of the line of Fig. 1 working first at 1 atm., then at 0.5, at 0.25 atm., and so down to as low pressures as may be practicable. The temperature corresponding to the intersection will change somewhat with the pressure, but will appear to be approaching a limit at about -273.13 as the pressure approaches zero. This limit we shall take as correct. Similarly, any other temperature may be repeatedly measured at progressively decreasing pressures, and the limiting value corresponding to zero pressure will give the correct temperature.

The absolute temperature defined in thermodynamics in terms of heat quantities is believed to be the same as that defined in this way with reference to gases.

The difference between the readings of a correct mercury thermometer and a good gas thermometer can be found in reference books such as "International Critical Tables," and the German Landolt-Boernstein Tabellen. Between 0 and 100°C . the difference seldom exceeds 0.1° for a correct mercury thermometer of the best glass.

12. Gas Mixtures.—When gases at the same temperature and (not too high) pressure are mixed, the final volume at this temperature and pressure is equal to the sum of the volumes of the separate gases. This law holds even better than the ideal gas

law itself. It may not hold if chemical reaction takes place. Combining both laws we obtain

$$V = \frac{RTn_1 + RTn_2 + RTn_3 + \text{etc.}}{p}, \quad (7)$$

or

$$pV = RT(n_1 + n_2 + n_3 + \text{etc.}), \quad (8)$$

where $n_1, n_2, \text{etc.}$, are the numbers of moles of gases of kind 1, 2, etc. We can express this by saying that the simple equation $pV = RTn$ holds even for gas mixtures, when n is taken to include the total number of moles of all kinds. Equation (8) can be written in another way:

$$p = \frac{RTn_1}{V} + \frac{RTn_2}{V} + \frac{RTn_3}{V} + \text{etc.} \quad (9)$$

This equation means that the pressure of a gaseous mixture is equal to the sum of the pressures which would be exerted by the gases put one at a time in the given volume V at the given temperature.

Kinetically the terms RTn_1/V , etc., may be interpreted as partial pressures, the total pressure being thought of as being shared by the different kinds of gas. This splitting up of the total pressure is not generally legitimate, and is permissible only when we adopt the simple kinetic picture or the simple theory of gases.

Equation (9) is frequently called Dalton's law of partial pressures, but Dalton's thought involves essentially the idea of equilibrium as taken up next.

13. Gas Mixtures in Equilibrium with a Pure Gas.—There are experimental methods by which we can study the equilibrium of a gas mixture phase with a pure gas phase with reference to the particular change: transfer of molecules of the pure gas from either phase to the other. In the logical analysis of these methods it becomes necessary to consider the idealized system represented by Fig. 2. This represents two compartments, both at the same temperature, separated by a so-called semi-permeable membrane. In the present case this membrane is

imagined capable of admitting the free passage of molecules of gas 1 in either direction while being gas-tight to the molecules of the other gases 2, 3, etc.¹ Platinum and especially palladium are permeable to hydrogen at high temperatures while being impermeable to nitrogen and other gases.

Our simple kinetic picture assumes that the gas molecules of the mixture, whether like or unlike molecules are considered, move independently of one another. Hence it will lead us to expect in this case that the molecules of kind 1 will be distributed at equilibrium similarly in both compartments, notwithstanding the presence of the gases 2, 3, etc., in the right-hand compartment. That is, there will be the same number of molecules of gas 1 per cubic centimeter on either side at equilibrium; n_1/V , the number of moles per unit volume, called the density or usually

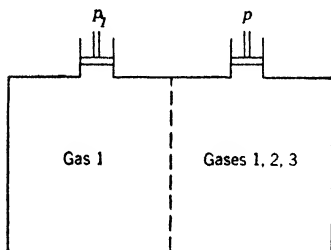


FIG. 2.—The equilibrium pressure p_1 .

concentration when a mixture is considered, is the same. The pressure p_1 of the pure gas is therefore equal to RTn_1/V , where n_1 may be taken as the number of moles of gas 1 in the mixture and V as the volume of the mixture. But RTn_1/V is the partial pressure of gas 1 in the mixture; that is, the pressure which the molecules of gas 1 in the mixture

would exert in the volume of the mixture were the other gases absent. Because p_1 is equal to this partial pressure, according to this simple theory, some authors call p_1 itself the partial pressure.

Furthermore, let x_1 be the mole fraction of gas 1 in the mixture, that is, $n_1/(n_1 + n_2 + n_3 + \text{etc.})$, and let p be the pressure of the mixture. Then from Eq. (9), which may be written

$$p = \frac{RT}{V}(n_1 + n_2 + n_3 + \text{etc.}), \quad (10)$$

¹ The phase rule does not apply to such systems containing selectively permeable membranes, considered as a whole, as the phase rule implies there is only one pressure in the system. But the phase rule may be applied without modification to the contents of any one compartment.

and the relation just discussed,

$$p_1 = \frac{RT}{V} n_1, \quad (11)$$

we have

$$p_1 = p \left(\frac{n_1}{n_1 + n_2 + n_3 + \text{etc.}} \right) \quad (12)$$

or

$$p_1 = px_1. \quad (13)$$

This is a very important form of the law governing the distribution of a gas between two phases. It expresses that the tendency of a gas in a mixture to push out through a membrane is proportional to the total pressure and to the mole fraction of the gas in the mixture. Because the product px_1 is equal to p_1 and to RTn_1/V according to the simple theory, some authors call the mathematical product px_1 itself the partial pressure.

In order to be able to refer in words to the pressure p_1 , we shall call this pressure p_1 of a pure gas 1 in equilibrium with a mixture with respect to transfer of gas 1 *the equilibrium pressure of gas 1 in the mixture*. This phrase implies that the pressure p_1 may be conceived as a property of the mixture, which implication will be justified in Chap. VI.

According then to the simple theory of gases and gas mixtures, the equilibrium pressure of a gas in a mixture is equal to the pressure of the mixture multiplied by the mole fraction of the gas in the mixture.

14. Accuracy of the Simple Theory of Gases and Improvements.—The ideal gas equation can be trusted to calculate the pressure, density, or temperature with an accuracy of about 1 per cent in the cases where the biologist is likely to be interested, since the pressure will rarely exceed 1 atm. When a more exact value is needed, gas densities at 0° and 1 atm., and pV products at different temperatures and pressures relative to the value of the pV product at 0° and 1 atm., can be found in "International Critical Tables," Vol. 3. There are times when an equation is necessary. A recent equation is that of Beattie and Bridgeman:

$$p = RTd + \left(RTB_0 - A_0 - \frac{Rc}{T^2} \right) d^2 + \left(A_0a - RTB_0b - \frac{RB_0c}{T^2} \right) d^3 + \left(\frac{RB_0bc}{T^2} \right) d^4, \quad (14)$$

where d is the molal density, and A_0 , B_0 , a , b , and c are constants, different for each gas, the values of which are given in Table I.¹

TABLE I.—CONSTANTS IN AN EQUATION OF STATE FOR VARIOUS GASES

Gas	A_0	B_0	$10^{-4}c$	a	b	Molecular weight
He.....	0.0216	0.01400	0.004	0.05984	0	4
Ne.	0.2125	0.02060	0.101	0.02196	0	20.2
Ar.	1.2907	0.03931	5.99	0.02328	0	39.91
H ₂	0.1975	0.02096	0.0504	-0.00506	-0.04359	2.0154
N ₂ and CO.....	1.3445	0.05046	4.20	0.02617	-0.00691	28.016 and 28.000
O ₂	1.4911	0.04624	4.80	0.02562	0.004208	32
Air.....	1.3012	0.04611	4.34	0.01931	-0.01101	28.964
Methane.....	2.2769	0.05587	12.83	0.01855	-0.01587	16.0308
Ethylene.	6.1520	0.12156	22.68	0.04964	0.03597	28.0308
CO ₂ and N ₂ O.....	5.0065	0.10476	66.00	0.07132	0.07235	44.000 and 44.016
Ethyl ether.....	31.278	0.45446	33.33	0.12426	0.11954	74.077
Ammonia.....	2.3930	0.03415	476.87	0.17031	0.19112	17.0311

The value of R to be used with these constants is 0.08206 liter-atm. (normal) per degree Centigrade and per mole, and $T = t + 273.13$. Hence the molal density is to be in moles per liter, and the pressure in atmospheres. Note that the figures entered in the fourth column have to be multiplied by 10,000 to give the values of c . The values for air are for dry air, free from carbon dioxide.

At reasonably low pressures the terms of Eq. (14) in d^3 and d^4 may be omitted, leaving the relatively simple equation

$$p = RTd + \left(RTB_0 - A_0 - \frac{Rc}{T^2} \right) d^2. \quad (15)$$

This equation is especially useful for ascertaining whether the ideal gas equation is accurate enough for a given purpose. It

¹ These are from J. A. Beattie and O. C. Bridgeman, *Proc. Am. Acad. Arts Sci.*, **63**, 229 (1928); *J. Am. Chem. Soc.*, **50**, 3133, 3151 (1928); and *Z. Physik.* **62**, 95 (1930). For an equation for the direct calculation of the volume or density see J. A. Beattie, *Proc. Nat. Acad. Sci.*, **16**, 14 (1930).

is to be noted that at very low pressures the term in d^2 also becomes small compared with RTd , and Eqs. (14) and (15) then give the same pressures as the ideal gas equation.

In order to calculate the density corresponding to a given pressure and temperature by the use of Eq. (14) or (15) it is most convenient to try a value of the density to see whether the corresponding pressure equals the given pressure; if not, the trial value is adjusted until the corresponding pressure calculated from it is found to be correct. At low pressures the density may also be calculated by means of the approximate equation

$$\frac{1}{d} = \frac{V}{n} = \frac{RT}{p} + B_0 - \frac{A_0}{RT} - \frac{c}{T^3}. \quad (16)$$

Turning back to Table I, the substances from ethylene down are condensable, that is, they can be liquefied by pressure without cooling below the temperature of melting ice. The gases above are relatively permanent, that is, pressure alone fails to liquefy them unless they are cooled. Owing to the large values of A_0 and c for the condensable gases the coefficient of d^2 comes out rather large (and negative), so that the correction on the ideal gas equation at 1 atm. and $0^\circ\text{C}.$, which is only 0.1 or 0.2 per cent for the permanent gases, reaches nearly 0.7 per cent for the biologically important carbon dioxide. At room or body temperature the correction will be somewhat smaller.

It has been found that Eq. (14), or its approximate form Eq. (15), gives also very good results when applied to gaseous mixtures. In this case we must understand by d the average density, that is, the total number of moles of all kinds per liter of mixture. Also, we must use values of the constants A_0 , B_0 , a , b , and c computed for the mixture according to its composition. The rule for this computation is simple. For the constants B_0 , a , and b we use an equation like the following:

$$B_0 \text{ (for the mixture)} = B_{01}x_1 + B_{02}x_2 + B_{03}x_3 + \text{etc.}, \quad (17)$$

where B_{01} signifies B_0 for gas 1, and x_1 its mole fraction. In the case of the constant A_0 , we must first find the square roots of the constants for the various gases, $A_{01}^{1/2}$, $A_{02}^{1/2}$, etc., and find then the square root of A_0 for the mixture according to the equation $A_0^{1/2} \text{ (for the mixture)} = A_{01}^{1/2}x_1 + A_{02}^{1/2}x_2 + A_{03}^{1/2}x_3 + \text{etc.} \quad (18)$

According to recent information the constant c should be computed like A_0 .

Problems

1. (a) Show that Eq. (4) contains Boyle's law; (b) also the law of Avogadro. (c) Find from it how the pressure changes with the temperature at constant density.

2. Find the value of k in the following equation for oxygen gas:

$$pV = kmT,$$

where m is the number of grams of oxygen in the volume V . Do not change the units atmospheres, liters, and degrees Centigrade. Start with the value 0.08206 given for R and use the system recommended. Hint: think of the molecular weight as 32 grams oxygen per mole.

3. Equation (6) can be simplified to $c^2 = 3RT/M$, by eliminating N , m , and n . Using this equation and the value of R in the c. g. s. system, 8.315×10^7 ergs per degree C. and per mole, calculate the mean velocity of hydrogen gas molecules at 0°C . to two or three significant figures. Use the system and show how all extra units cancel out, leaving $\text{cm.}^2/\text{sec.}^2$ for c^2 . Finally find the velocity in miles per second, using the conversion factor 1.6093×10^6 cm./mile. *Ans.* 1.1425 miles/sec. Hint: the erg is equivalent dimensionally to $\text{cm.}^2\text{-gram/sec.}^2$, as may be seen at once by those who remember the dimensions of acceleration as l/t^2 , and the relations: erg is unit of work, work is force times length, force is mass times acceleration.¹ The number 3 in the equation is a pure number, that is, it needs no specification of units.

¹ Those familiar with the calculus should note that acceleration is d^2l/dt^2 , and that the dimensions of dl and of higher differentials such as d^2 are the same as those of l itself, because all differentials may be regarded as differences, and the difference of, say, apples is still apples. But dt^2 has the dimensions of the square of the time.

CHAPTER III

GENERAL PROPERTIES OF LIQUIDS AND SOLIDS

Simple equations of state for liquids and solids cannot be given. Every individual liquid and solid would have its own equation. Fortunately, the effects of pressure and temperature on the density of liquids and solids are much smaller than in the case of gases, and for many purposes the density may be assumed constant. When account must be taken of these effects, use is generally made of the compressibility and the coefficient of expansion, which may usually be assumed constant. The compressibility is the fractional decrease of volume per unit increase of pressure, and the coefficient of expansion is the fractional increase of volume per unit increase of temperature.

When these quantities themselves may not be considered constant they are defined in terms of the differential calculus as $-(dV/dp)_T/V$ and $(dV/dT)_p/V$, respectively, where the subscripts indicate the variable that is not changed.

The properties of solids are as a rule not quite so definitely reproducible as those of liquids or gases. Thus, the density of copper depends not alone on the pressure and temperature, but also somewhat on its state of strain, and the density of soft copper can be increased by hammering. Furthermore, some of the physical properties of crystals can be different in the three directions of space. Such effects, which are usually small, are ignored when we apply to solids the phase rule or other laws relating to equilibrium to be developed later. Another effect which is also ignored is that due to surface tension, which effect is appreciable only when the solid or liquid is very finely divided, or the liquid is in a narrow tube.

15. Viscosity of Liquids.—Viscosity is a measure of the transfer of momentum per second, or the force, required to produce a given velocity of flow in a liquid relative to the walls of the tube in which

it flows. It may be said to measure the internal friction of liquids. The viscosities of different liquids can be compared by measuring the times required for equal volumes to flow through narrow tubes under the same pressure condition; indeed, the viscosities are then directly proportional to the times. The viscosity is denoted by the Greek letter eta (η). If t_1 and t_2 are the times required for two liquids, whose densities are d_1 and d_2 , to flow out of a tube with a small orifice (or to flow from one mark on the tube to a lower mark), we have to allow for the fact that the liquid whose density is greater is subject to a greater force of gravity. The following equation takes care of this:

$$\eta_1/\eta_2 = t_1 d_1/t_2 d_2. \quad (1)$$

When bodies move without friction, the application of a constant force increases the velocity continuously, but in the viscous flow of fluids a constant force brings about very soon a certain velocity which does not change if the force remains constant. If the viscosity of one liquid is known at the given temperature, that of the other can easily be found from Eq. (1) after measuring the times.

Water is often taken as a standard, and its viscosity assumed unity for whatever temperature obtains. The result thus calculated for the other liquid is called its relative viscosity.

The viscosity of all liquids decreases with rising temperature, a behavior opposite to that of gases. The molecules of liquids are much closer together than those of gases, and very much under the influence of one another. This influence evidently varies with temperature.

A possible benefit to the individual ill with fever has been seen in the decrease of viscosity of the blood due to the rise of temperature, which reduces the work required of the heart to produce a given volume of circulation.

16. Refractive Index.—The angle, through which a ray of light is bent on entering a liquid from the air, depends on the refractive index n .

In Fig. 3 the angle of the incident ray is designated by i , and that of the refracted ray by r . Both angles are measured from the normal to the surface (that is, the line perpendicular to it).

The relation is

$$n = (\sin i)/(\sin r), \quad (2)$$

where n is the same for all values of i and r , but depends somewhat upon the wave length of the light. The index can be measured by measuring angles in a refractometer. An instrument requiring but very small quantities of liquid is the Pulfrich refractometer. Monochromatic light is generally used, for instance, that from a sodium flame. The symbol n_D means that sodium light was used, the subscript referring to the prominent D line of the sodium spectrum.

The light used for measuring the refractive index has no appreciable effect on the liquid, and the index is definite when the state of the liquid is fixed by fixing the temperature, the composition, and either the pressure or the density. By measuring the refractive index, valuable aid is gained in the identification of pure liquids; if the liquid is known, information as to its purity can be obtained. Finally, the percentage composition of a mixture of two components (a binary mixture) can sometimes be determined.

For a large number of substances the value of n is fixed by the value of the density alone, and is affected by the temperature only in so far as this affects the density. The expression which relates the values of n and d is the Lorenz-Lorentz equation

$$\frac{n^2 - 1}{n^2 + 2} \times \frac{1}{d} = \text{a constant}, \quad (3)$$

where the constant is different for different substances, but is independent of the temperature or density. The ordinary density in grams per cubic centimeter is usually understood by d , and multiplication of the constant by the molecular weight gives the so-called molal (or molecular) refractivity of the substance.

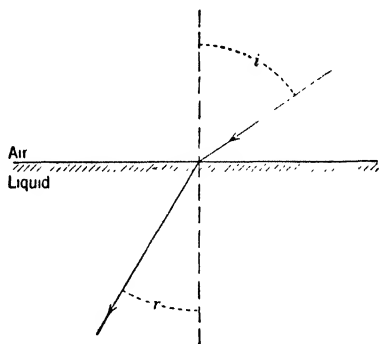


FIG. 3.—The index of refraction is $\sin i/\sin r$.

The effect of increasing the molecular weight by the addition of CH_2 groups to organic molecules, on the molal refractivity, on the molal volume, and on other physical properties, has been extensively studied. Regularities are usually observed in homologous series, especially if the first member of the series is left out of consideration, and the effects of marked changes of constitution, such as that due to the introduction of a double bond, have been noted.¹

17. Liquid Crystals.—Many substances are known which can be brought into the state of a liquid crystal. Nearly 200 such substances are listed in "International Critical Tables,"² Substances in this state are usually opalescent, although not consisting of emulsion or mixture. The opalescence is due to a tendency of the molecules to orient themselves relatively to their neighbors. When liquid crystals are placed between glass plates the molecules often become oriented with respect to the glass, especially if the liquid is rubbed between the plates in a thin layer. When the plates with their layer of liquid are then placed between crossed Nicol prisms in a polarizing microscope (the preparation being maintained at a suitable temperature) various patterns may be viewed, due to double refraction.

The liquid crystals are liquid from a mechanical standpoint. When one is heated to a certain temperature it melts to a clear liquid, in which the tendency towards orientation is entirely overcome by the motion of the molecules. At a certain lower temperature it changes to solid crystals. Liquid crystals are to be regarded as substances in a special phase, which is stable (at atmospheric pressure) between two definite temperature limits—the (upper) melting point and the (lower) transition point. The temperature range is often restricted to a few degrees, and often occurs at 80° or above.

Numerous salts and esters of the biologically important cholesterol have been brought into the state of a liquid crystal.

Liquid crystals are also called anisotropic liquids. This means that their properties are not the same in all three directions of space.

¹ SMILES, SAMUEL, "The Relations between Chemical Constitution and Some Physical Properties," Longmans, Green & Co., New York, 1910.

² Vol. 1, p. 314.

CHAPTER IV

SURFACE TENSION

Surface tension is often treated as a property of liquids, though it is really a property of the boundary of the liquid and cannot be given an exact value without stating what other phase, be it gas, liquid, or solid, lies on the other side of the boundary.

18. Definition and Measurement.—Surface tension is defined as the force per unit length on *any* line lying in the surface and is directed along another line lying in the surface and perpendicular to the first line. Both these lines may be curved, when the surface is curved. Consider a stretched membrane of rubber. If this be slit along any line, the rubber will draw away from the line. Before the cut was made along the line, there was evidently a force perpendicular to the line, holding the rubber together. The magnitude of the force is evidently proportional to the length of the line. This illustrates the meaning of the lines used to define surface tension.

In a drop of water there exist forces perpendicular to all possible lines in the surface, although they cannot be so easily demonstrated. The surface tension acts in the direction to contract the surface. There is an important difference between the surface tension of a liquid and the tension in a stretched rubber band, for, within limits, the tension in the band is greater, the more the band is stretched, whereas the surface tension is quite independent of the area of the surface, so long as the temperature and composition are kept constant.

Because of the contractive surface tension the pressure within a soap bubble or a drop of water is greater than the pressure without. This pressure is however minute, compared with the so-called *internal pressure* of liquids, which is defined in a variety of ways by different authors. All agree that it is enormous; it exists in a liquid whose surface is plane; and it is due, like surface tension, to the mutual attraction of the molecules of the liquid.

If we consider the rise of a liquid in a capillary tube we can find a line of particular importance, along which the tension acts perpendicularly. Figure 4 represents in section a capillary tube dipping into a liquid contained in a wide vessel. It is only when a liquid wets the tube that it rises in the capillary; otherwise it sinks, owing to its tendency to contract. For wetting, it is necessary that the liquid should adhere more tightly to the tube than it coheres to itself. A consequence of the wetting is that a film of liquid extends up the walls of the tube much higher than the practical height h of the little column above the free surface, and sticks firmly. The contractive action of surface

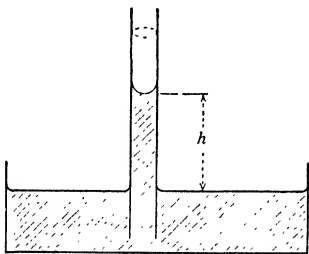


FIG. 4.—Rise of a liquid in a capillary tube.

tension therefore tends to shrink the liquid up into the capillary until it is balanced by the weight of the column. Somewhere above the column, but within the adhering film, we may locate our reference line, which is a circle as shown by the dotted line. If the radius of the tube is r cm., the circumference of the line is $2\pi r$ cm., and the force perpendicular to it is $2\pi r\gamma$ dynes, where γ (Greek gamma) is the surface tension in dynes per centimeter. The dyne is a very small unit of force. It is about the weight of a milligram, about one-twentieth the weight of a house fly.

The area of the little surface bounded by this line is πr^2 , and the volume of the column is $\pi r^2 h$ if we measure h up to the average height of the curved meniscus. If the density of the liquid is d , the mass of the column is $\pi r^2 h d$ and the gravitational force upon it is $\pi r^2 h d g$, where g is the so-called acceleration of gravity, or the gravitational force on one gram. The value of g is about 981 dynes per gram.

Now at balance, the force along the line due to surface tension is equal to the gravitational pull on the column, that is,

$$2\pi r\gamma = \pi r^2 h d g. \quad (1)$$

Hence,

$$\gamma = (r h d g)/2. \quad (2)$$

This equation is used to calculate the surface tension from the capillary rise.

In another method, elaborated by du Noüy, the experimenter determines on a very sensitive spring balance the force necessary to tear a film of liquid which has been pulled up from the surface by a platinum ring of known radius. The film just before being torn apart has a shape much like that of a napkin ring, as indicated in Fig. 5, so that two surfaces are involved, inside and outside. The force required is therefore twice $2\pi r\gamma$.

A relative method much used for measuring surface tension is the drop-weight method. If r is the radius of the circle along which a drop breaks away when the liquid is caused to run very slowly out of a small tube (Fig. 6), the weight of the drop is opposed at the moment of breaking by a surface tension of $2\pi r\gamma$ dynes. The weight of a drop may be found by counting the

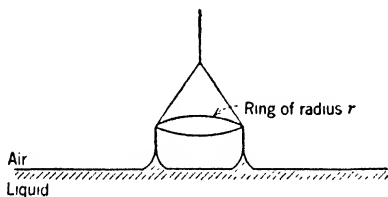


FIG. 5.—The ring method for surface tension.

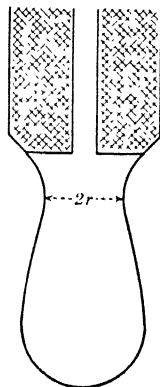


FIG. 6.—A drop falling from a ground and polished tip.

number of drops in a known weight of the liquid. The face of the tube is ground flat and smooth. The radius of the face of the tube is not necessarily equal to r , and r is therefore not easy to measure. With properly prepared tubes it is however justifiable to compare two different liquids, assuming r to be the same for both. The surface tensions of the two liquids are then proportional to the weights of a drop and therefore inversely proportional to the numbers of drops into which the same weight of the two liquids divides in the two cases. By using one liquid of known surface tension, the surface tension of another liquid can thus be determined.

In applying the drop-weight method it is sometimes more convenient to take an equal volume of the two liquids. Then the weights taken per cubic centimeter are as d_1 and d_2 (the densities) and if the numbers of drops per cubic centimeter be n_1 and n_2 the weights of the drops will be as d_1/n_1 and d_2/n_2 . The two surface tensions can be compared by use of the equation

$$\frac{\gamma_1}{\gamma_2} = \frac{d_1/n_1}{d_2/n_2}. \quad (3)$$

19. Some Results of Measurements of Surface Tension.—The surface tension of liquids varies considerably with the temperature, becoming smaller at higher temperatures. It will finally become zero when the temperature is raised as far as the so-called critical temperature, at which point a liquid and its vapor become indistinguishable. The relation between surface tension and temperature is practically linear over a considerable range of temperature, and if the best straight line through a plot of surface tension against temperature is extended (far beyond the measured points) it usually indicates that the surface tension becomes zero at about 6°C. below the critical temperature.

Hence the best line through the points is not really straight.¹ The change of surface tension per degree Centigrade is for many substances proportional to the two-thirds power of their molal volumes (the law of Eötvös).

Various methods of measuring surface tension usually agree when applied to pure liquids, but often do not agree when applied to solutions or mixtures. One reason for this is the following:

As Gibbs showed, if a substance lowers the surface tension of a liquid when dissolved in it, then the concentration of the substance in the surface film is greater than in the bulk of the liquid. The effect is opposite for substances, such as salts, which increase the surface tension of water, but the effects are then smaller, as no substances very greatly increase the surface tension of water. Now when fresh surfaces are formed in the measurement of surface tension, an interval of time may be required before the concentrations in the film assume their equilibrium values, in

¹ An article (in English) by Katayama, *Sci. Repts. Tôhoku Imp. Univ. Japan*, **4**, 373 (1915), may be consulted for an improved equation relating surface tension to temperature.

which case rapid methods will not give the same results as slow methods, as the surface tension must depend on the surface concentration.

Gibbs gave an exact equation for calculating the effect, but the difficulties of evaluating some of the quantities occurring in it¹ have prevented quantitative experimental verification of the equation, save in one or two exceptional cases. The measured effects are, however, even greater than those calculated (from a simplified equation) and the "Gibbs adsorption" is of great importance in biology.

Of pure liquids, water has an unusually high surface tension. Yet it is only about 72 dynes per centimeter at 25°, and we have noted how small is the force of a dyne. How can such small forces have importance in biology?

If we consider a series of spheres (or cubes) of progressively decreasing size, we find that as the radius of the sphere is halved the area is decreased to one-fourth, and the volume and hence the weight to one-eighth of its value. Therefore the surface and the various effects of surface tension become more and more important compared to the weight as the organism or part of it becomes smaller. Thus, light insects cannot escape from a water surface, if wetted, but some ride with ease on water, being protected against wetting by a film of oil or grease.

When such substances as soap, saponin, bile or bile salts are dissolved in water the surface tension is greatly decreased. Such substances are called surface active or capillary active.

According to Traube's rule, when we compare the members of a homologous series of organic compounds (differing by the progressive addition of a CH_2 group) we find the effect on the surface tension to increase by a factor of 3 from each member to the next higher, so that an equal lowering of the surface tension is produced by taking a diminishing series of concentrations, each one only one-third of the preceding concentration in moles per liter.

We are therefore not surprised to find that the many substances of high molecular weight present in the fluids of the animal body give these fluids surface tensions considerably less than that of water, in the case of bile as low as two-thirds that of water.

¹ The chemical potential or the "activity."

When sampling biological fluids for analysis, or before measuring suspensions of red blood cells, it is of course necessary to make sure first that the fluid or suspension is thoroughly mixed. It would, however, be unpardonable to shake to the point of froth production, as this might seriously lower the concentration of important surface-active substances in the bulk of the fluid.

20. Mutual Surface Tension of Liquids.—Liquids are sometimes soluble in one another only to a limited extent, as carbon tetrachloride and water. When two such liquids are shaken together, and any emulsion permitted to break up, they will be separated by a surface, or interface. This surface will have a surface tension, just like the surface of a liquid in contact with air or its vapor. It is called the mutual or interfacial surface tension. Most of the methods for measuring surface tension have been adapted to the measurement of mutual surface tension.

Such liquids can often form emulsions, consisting of drops of one liquid (the dispersed phase) in the other (the continuous phase). The stability of emulsions can be greatly affected by the addition of other substances. From two pure liquids it is rarely or never possible to prepare a stable emulsion without the addition of some other substance. The addition of substances soluble in one or both of the two liquids may affect the stability favorably or adversely; addition of insoluble, finely divided solids may serve to impart stiffness and practical stability to emulsions. Milk may be regarded as an emulsion of fat in water; butter, as one of water in fat. The theory of emulsions depends heavily on our knowledge of mutual surface tension, as does also the explanation of the physicochemical behavior of living cells, which are of that small order of size in which capillary effects are very great.

If we know the surface tensions of the two liquids when each is "saturated" with the other (that is, each has been dissolved in the other, by shaking them together, until equilibrium has been obtained at the given temperature) we can calculate their mutual surface tension by means of *Antonoff's rule*. This states that the mutual surface tension equals the difference between the two surface tensions of the saturated liquids, each measured in contact with the mixed vapor in equilibrium with the liquids (in contact with the "saturated vapor"). All surface tensions are positive,

and for Antonoff's rule the difference is found by subtracting the less from the greater surface tension. In practice, surface tensions measured when the liquid is in contact with air are often nearly equal to those measured with the saturated vapor.

We can better understand this rule by reference to Fig. 7 and the following discussion, which brings out the connections between the rule and two other rules, one for the spreading of one liquid on another, and one for the stability of emulsions.

To illustrate the general principles we shall choose the special case of carbon tetrachloride and water. A subscript 1 will refer to carbon tetrachloride, a subscript 2, to water; thus γ_1 designates the surface tension of carbon tetrachloride, and γ_2 , the surface tension of water. The mutual surface tension we shall designate by γ_{21} (read sub 2-1, not 21). Carbon tetrachloride has by far

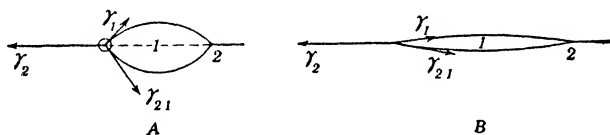


FIG. 7.—Liquid of lower surface tension (1) spreading on liquid (2). A, B, successive stages.

the lower tension. The values at 20° are γ_1 , 26.66; γ_2 , $72.75 \pm .05$; and γ_{21} , $45. \pm 1$, in dynes per centimeter.¹

If a very small drop of carbon tetrachloride is placed on a water surface, the drop will flatten and spread out until the water surface is entirely covered or the film has become extremely thin. An early stage in this spreading may be represented, in cross section, by Fig. 7a. The carbon tetrachloride at the top of the drop is in direct contact with the air, not being covered with a film of water; at the bottom of the drop it is in direct contact with the water. There are therefore three surfaces with the surface tensions γ_1 , γ_2 , and γ_{21} . These three surfaces meet at a ring around the drop, the ring being indicated in cross section by the broken line. If a pin be held perpendicular to the plane of Fig. 7a at the spot indicated by the small circle, it will have the direction of the ring at the point where the pin would pierce the paper. We take this ring as the reference line because it lies in all three surfaces, and the forces of surface tension must lie in

¹ "International Critical Tables," Vol. 4, p. 432.

their respective surfaces and be perpendicular to the ring, that is to say, to the pin. These forces are represented by the arrows labeled γ_1 , γ_2 , and γ_{21} . They are in the proper direction to *contract* the surfaces.

When the drop is very small we may neglect its weight in comparison with the surface tensions. Now, since we are discussing the case in which the drop spreads, it is evident that the pull of γ_2 on the ring exceeds the combined pull of γ_1 and γ_{21} in the exactly opposite direction. This will be the case even when, according to Antonoff's rule, γ_2 equals the sum of γ_1 and γ_{21} , because, with the angles as shown, the full forces of the latter tensions are not felt against γ_2 , but only their projections on the line in which γ_2 lies, which projections are necessarily shorter than the forces themselves. But as the drop spreads out and becomes extremely thin, the picture will be more like that of Fig. 7b. Here γ_1 and γ_{21} are more nearly in the same line with each other and with γ_2 . When spreading is over, all the forces will lie in the same line, and for balance we must have

$$\gamma_2 = \gamma_1 + \gamma_{21}, \quad (4)$$

which is Antonoff's rule.

Consequently, when either liquid is capable of spreading on the other, Antonoff's rule must hold, at least in the limiting case of an extremely thin layer, and, furthermore, the liquid which spreads is the one with the lower surface tension. The fact that the rule is actually found to hold in experiments involving relatively thick layers is evidence that the surface tension does not depend on the thickness of the films of liquid; which is what we should expect, so long as the film does not become so thin as to change in character. Some liquids cease to spread when the film is still some thousands of molecules deep. Such a film is thin enough for the forces to lie in practically the same line, and thick enough for the surface tension to have the same value as in thicker films.

Other liquids are believed to continue to spread out until the layer is only one molecule deep. Such a case is not a suitable one to consider for the purpose of deriving¹ Antonoff's rule, as the

¹ Experienced students do not ordinarily consider derivations as proofs of fact, but rather as aids to the understanding of facts and their mutual relations.

surface tension of a film one molecule deep, if indeed it is a fit subject for discussion, is very likely not the same as that of a thick layer. The theory given above, while it enables us to understand from Antonoff's rule some of the facts about spreading, does not explain why some liquids cease to spread when the layer is many molecules deep and other liquids continue to the possible limit, as the theory does not take into account the special forces which molecules can exert on one another when they are oriented in special ways.

If a small drop of water is placed on the surface of carbon tetrachloride we may have at first a picture like Fig. 8a. But now since γ_2 the surface tension of water is the greater, and by Antonoff's rule equal to $\gamma_1 + \gamma_{21}$, the tension γ_2 is greater than the components of γ_1 and γ_{21} along the line in which γ_2 lies, so

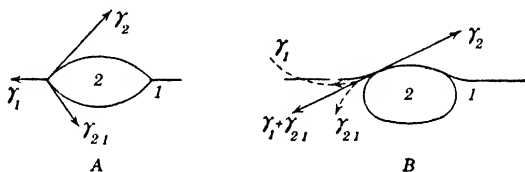


FIG. 8.—A small drop of liquid of higher surface tension (2) forming a lens on liquid (1). A, B, successive stages.

that γ_2 pulls the ring up and the drop of water shrinks up into a so-called lens on the surface of the carbon tetrachloride. If the weight of the drop is insignificant the shrinking ceases when γ_1 and γ_{21} lie in the same straight line as γ_2 , but oppositely directed, as indicated in Fig. 8b. If the weight of the drop is important (or its buoyancy), the tensions may not all lie in the same line, and the sum of the three components of tension plus the component of the pull of the weight must equal zero.

It is observed that when liquid 1 spreads on liquid 2, liquid 2 will not spread on liquid 1, but shrinks up into a lens. It might be supposed that because liquid 2 can form a lens on liquid 1, liquid 1 cannot possibly form a lens on liquid 2, but this has by no means been shown. There appears indeed to be no reason why, in the case of a heavy drop, the weight of the drop may not balance the tendency of the drop to spread. Figure 9 shows a possible arrangement of the forces in such a case. Here the

effectiveness of γ_1 and γ_{21} is lessened because of the angles, but this is compensated by the component of force due to gravity. The author believes he has observed lenses of carbon tetrachloride on water much like Fig. 9. When the bottom of the drop was detached, thus lessening the weight, the drop was seen to spread.¹

Throughout the above discussion it was supposed that the two liquids were saturated with each other. In the particular case of carbon tetrachloride and water the surface tensions of the liquids do not change much when they become saturated, but in general we need not expect the rule of Antonoff to hold unless the values of γ_1 and γ_2 refer to the saturated solutions. Unfortunately,

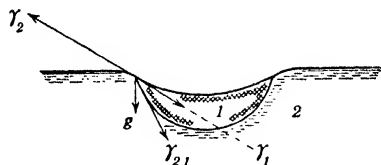


FIG. 9.—Exceptional lens formation: CCl_4 (1) on H_2O (2); g represents the force of gravity (not to scale).

most of the experiments on spreading have been performed without care to secure saturated liquids, but the surface layers may of course have become nearly or quite saturated during the observations.

In many cases the facts of capillarity are open to question, and the theoretical discussions open to argument. Difficulty is experienced in obtaining sufficiently clean surfaces for experiment. Another difficulty is due to our ignorance of the values of the angles mentioned above, the angles of contact. These are very difficult to measure, and in theoretical discussions they are often considered to be 0 or 180 deg., so that all the forces lie in the same line.

Thus according to a theory of spreading often given, spreading will occur if, and only if, $\gamma_2 > \gamma_1 + \gamma_{21}$. We also should obtain this result by assuming that all three forces of Fig. 7a act in the same line. This theory, put forward before the discovery of Antonoff's rule, depends upon a violation of it and is therefore unsatisfactory.

It has also been suggested that some correction, admittedly small, ought to be applied to Antonoff's rule for the weight of a drop. According to the discussion given above, the exactness of the rule would have nothing to do with the weight of any drop.

¹ The lenses were produced by judiciously shaking and swirling a bottle containing a few inches of carbon tetrachloride under a like layer of water and a generous air space. The bottom of the drop could be detached by means of a bent wire.

In spite of these difficulties it is agreed that a high surface tension of liquid 2 favors the formation of lenses on liquid 1, and that a low surface tension of liquid 1 favors its spreading on the surface of liquid 2. It is also agreed that Antonoff's rule is nearly or quite exact for many pairs of liquids; the only exceptions relate to amalgams.

21. Emulsions.—Consider now an *emulsion* consisting of drops of water in a continuous phase of oil. We may think of the oil as being spread over the surfaces of the water drops; indeed, we can imagine an emulsion being produced by taking a great number of water drops, coating each with a film of oil, and immersing the coated drops in liquid oil. We should therefore expect, and it is found, that it is easier to produce a stable emulsion of liquid 2 dispersed in a continuous phase of liquid 1 than the reverse type of emulsion, when liquid 1 has the lower surface tension. Furthermore, since we must compare the surface tensions of the liquids when each is saturated with the other, we see that the addition of a third substance may act to favor one type or the other, according to which liquid experiences the greater lessening of surface tension as a result of the addition. When a limited quantity of the third substance is added, it is distributed between the two phases, the distribution usually favoring one phase or the other. Evidently the relative lowering of surface tension is greater for the water phase, when sodium salts are added, and is greater for the oil phase, when calcium salts are added, for sodium salts are found to favor the formation of oil-in-water emulsions, and calcium salts to favor the formation of water-in-oil emulsions. In a number of instances it has been found possible to produce one type of emulsion or its reverse, according to whether the ratio of sodium to calcium is greater or less than a certain critical value. Either type of emulsion could be inverted by adding the appropriate salt. At the critical ratio sometimes neither type of emulsion was stable, and sometimes, rather curiously, both types appeared to be stable even in contact with each other.

Sodium and calcium have long been regarded as antagonistic in biology. The phenomena involved in the clotting of blood have been interpreted in terms of emulsion reversal.

When a third substance is added to two pure liquids in order to prepare a stable emulsion it is likely to lower the surface tension at the interface. This is supposed to lower the tendency of the droplets to coalesce when they touch. When it so lowers the mutual surface tension it is furthermore concentrated, or "adsorbed," at the interface, in accordance with the rule of Gibbs. This is likely to form a protective film, which lends stability. The finely divided solids used in the manufacture of emulsions collect at the interface and add stability; solids are chosen which, having been wet by the liquid that is to be the continuous phase, are not easily wet by the droplets, as otherwise they would tend to break up the emulsion.

As the result of much ingenious experimentation with films there has been obtained considerable information on the orientation of the molecules at a surface, for which the reader may consult "An Introduction to Surface Chemistry," 2d ed., by E. K. Rideal, The Macmillan Company, New York, 1930.

22. The Electrical Potential at a Surface.—Surfaces, either plane or curved, are often electrified. The electric charges form a double layer, somewhat as in Fig. 10.

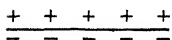


FIG. 10.—Double layer.

There is a change of potential at or near the surface, the effect of which can be observed when the surface is included in an electrical circuit. Sometimes the value of the change of potential is different according to the method used for measuring it. This indicates that the potential does not change with perfect abruptness, at a mathematical surface, but gradually builds up over an appreciable distance, so that different methods measure the potential at different places.

The surface tension is defined as the net force per centimeter, whether caused by molecular attraction alone or partly by electrical charges. The effect of the charges, as in Fig. 10, is to diminish the surface tension. The attractive forces between charges of unlike sign are exerted perpendicularly to the surface and are not felt in it, whereas the self-repulsion of the charges of like sign tend on both sides to draw out the surface.

23. Electrical Charges and Colloids.—Many emulsions, suspensions, and colloid solutions owe their stability to the electrical charges on the surfaces of the particles, and when anything is done

to lessen the electrical charge the tendency of the particles to coalesce when they touch becomes greater, often resulting in a separation of the particles from the continuous phase.

One way for a particle to acquire a charge is by the adsorption of an ion. When we add electrolytes to the medium, a particle already charged may have its charge changed by further adsorption. Particles may be discharged by the action of ions of the opposite sign, and are likely then to separate from the medium or to precipitate. Colloidal solutions can often thus be precipitated by the addition of electrolytes. As a rule, the ion of the electrolyte that has a sign opposite to that of the colloid is of principal importance. As a rule, the effectiveness of an ion increases rapidly with its valence.

Colloidal solutions of opposite sign often precipitate each other, when mixed in suitable quantities. The law of definite proportions holds approximately, if they are always mixed in quite the same manner. But if x cc. of colloid solution *A* are precipitated quantitatively by y cc. of colloid solution *B* when the y cc. is added all at once, then more than y cc. will probably be required if it is added in portions, each portion being well admixed.

If two colloidal solutions of opposite sign are mixed, one solution being in large excess over the quantity required for precipitation, it may happen that no precipitation takes place, but a colloidal solution remains, whose particles have the same sign as that of the colloid taken in excess.

Often a colloidal solution of little stability may be stabilized by the "protective action" of another colloid added to it. An example is colloidal silver, stabilized for therapeutic purposes by the addition of albuminous material.

Another way for a particle to acquire a charge—by dissociation as an acid or a base—will be discussed in Chap. XXII, Ampho-teric Electrolytes.

CHAPTER V

PHASE RELATIONS OF GASES WITH LIQUIDS AND SOLIDS FOR PURE SUBSTANCES

We have considered some of the more important properties of the gaseous, liquid, and solid phases, taken one at a time. When they are taken two or more at a time, the mutual phase relations are of still more interest.

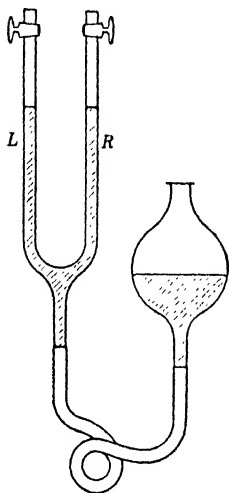


FIG. 11.—Vapor pressure experiment.

24. Vapor Pressure.—Figure 11 illustrates a simple apparatus, consisting of two glass parts, connected with flexible rubber tubing and partly filled with mercury. Any air between the mercury and the stopcocks may be largely removed by lifting the reservoir and forcing air out through the open stopcocks. By closing the stopcocks and lowering the reservoir, air bubbles sticking to the walls of the glass tubes may be dislodged and may then be forced out through the stopcocks. When we then close the stopcocks and lower the reservoir we shall find that the mercury levels stand at the same height, provided that the capillary depression of mercury is the same for both. If now some gas is introduced into the left-hand side *L*, the level in *L* will be lower than in *R*, and the more so if the reservoir is raised, since the volume of the gas in *L* is thereby decreased and the pressure must rise.

If instead of gas a drop of some pure liquid, such as water, is introduced into *L* with care to exclude air, the level in *L* will be lower than in *R*, as before, but it will be found on raising or lowering the reservoir that the difference of levels will be the same, irrespective of the heights of the mercury surfaces, as long as liquid water and space above it remain. The water vapor is

under a pressure proportional to the difference of levels. We have arbitrarily determined upon some temperature at which to experiment, and are not able to make the pressure what we please.

Now the weight of the drop may be kept too small to cause any appreciable difference in levels, so that the force acting on the left-hand mercury surface is due to the pressure of the water vapor formed by the evaporation of a little of the drop. The pressure is measured by the difference in heights of the two mercury surfaces (corrected for any difference due to capillarity) and is given by the formula taught in physics: $p = hdg$, where p is the pressure in dynes per square centimeter due to the weight of a column of fluid whose height is h and density d , g being the weight per gram. Other ways of stating pressure have been discussed in Chap. II.

In the above experiment the pressure is found to be independent of the combined volume of liquid and vapor, and therefore independent of the quantity evaporated, so long as the temperature of the room does not vary. This pressure, at which the liquid and its vapor are in equilibrium at a given temperature, is called the vapor pressure of the liquid at the given temperature. Although it is defined with reference to two phases, it is often conceived as a property of the liquid, and this conception will be justified later.

According to the phase rule the variance of such a system is 1, and fixing the temperature permits us therefore to measure the pressure. The densities also of the vapor and the liquid are fixed by the temperature, and are called the densities of the saturated vapor and of the saturated liquid. The total volume (of the combined phases) is however not fixed, and is never taken into account by the phase rule when more than one phase is present.

25. Vapor Pressure and Temperature.—The vapor pressure of liquids increases with the temperature, and the variation can be shown by a line on a diagram such as the line OC of Fig. 12. This is the vapor pressure line. Any point on the line, such as x , gives the pressure and temperature of liquid and vapor in equilibrium. Take for consideration some pure liquid, such as water, in equilibrium with its pure vapor at a temperature and corresponding pressure given by the point x . If we should decrease the volume occupied by the liquid and vapor without changing the temperature the vapor would condense, at first without changing the pressure. If we should continue to decrease the

volume the vapor would all condense and the pressure on the liquid would then increase until we ceased to compress it, when the pressure might be given by a point such as *L*. The liquid would now entirely fill the vessel and would not differ in appearance from a compressed gas. An opposite treatment would entirely vaporize the liquid, and the condition of the substance might be represented by the point *G*. From the history of this phase we are disposed to call it a gas (or vapor). Its variance

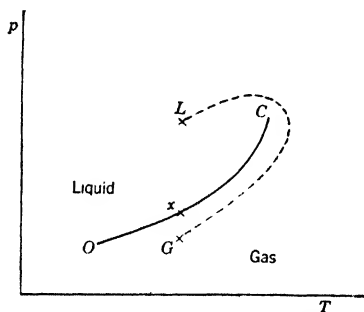


FIG. 12.—A vapor pressure line.

is, however, 2, and it is therefore possible to vary its pressure and temperature within reasonable limits as we please; we can for instance vary its temperature and pressure in accordance with the broken line, passing around the upper end *C* of the line and arriving finally at the point *L*.

The vapor pressure line does not extend upwards in-

definitely, but comes to an end at the critical point *C*. It is only along the line *OC* that liquid and vapor can be together in equilibrium. Hence the gas shows no signs of condensation when we take it from *G* to *L* around the critical point, and we should still call it a gas, from its history.

But the substance in the state represented by *L* is exactly the same, whether it has passed from *x* directly to *L* (and we call it liquid), or it has passed from *G* around the critical point to *L* (and we call it gas). The transformation represented by the broken line has been called the continuous transformation of gas into liquid, but it seems better to emphasize that it is impossible to distinguish gas from liquid unless both phases are present.

A distinction between gas and vapor was formerly made, according as it was impossible or possible to cause the appearance of liquid by more compression at constant temperature, but this distinction is often ignored today, as it has no particular scientific importance.

Inspection of Fig. 12 makes evident the correctness of the familiar definition of critical temperature, as the highest tem-

perature at which the gas can be liquefied by pressure alone (that is, by pressure at constant temperature).

26. The Triple Point.—At a lower temperature the line OC branches as shown in Fig. 13. Solids such as ice can evaporate directly without melting and come to equilibrium with the vapor phase. When water vapor condenses directly to ice, it is usually called frost. A solid has a definite vapor pressure at a given temperature just like a liquid. Its vapor pressure line (or sublimation line) is given by AO . Along AO ice and vapor can be in equilibrium without the presence of liquid. Only at one point O , where the two vapor pressure lines intersect, can we have liquid, solid, and gas together in equilibrium. The temperature and pressure are both fixed by nature, and are found, in the case of the substance water, to be about $+0.01^{\circ}\text{C}$. and 4.579 mm. ice-cold mercury.

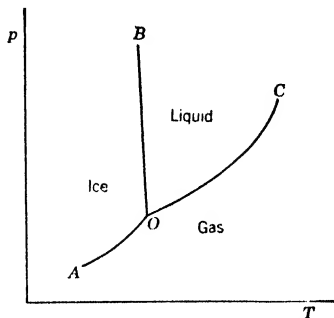


FIG. 13.—Phase diagram. Water near the triple point O .

Ice is in equilibrium with water at 0°C ., when under the pressure of the atmosphere. There is a difference of temperature of 0.0075° , due to the effect of 1 atm. of pressure on the melting point of ice. The line OB shows (with great exaggeration) how the melting point varies with the pressure. In the case of H_2O this line slopes upwards slightly towards the left. It is proved by the use of thermodynamics that this will be the case for any substance whose solid phase floats on the liquid. In most cases the solid phase sinks in the liquid. Such a substance is called normal, and the melting point is higher at higher pressures. The point O is called the triple point.¹

¹ There is a further difference of temperature of 0.0023° to be considered, which makes the temperature at the triple point more exactly $+0.0098^{\circ}$. This arises from the fact that Centigrade zero is according to the present convention the temperature of ice in equilibrium with water under the pressure of a normal atmosphere when the water is saturated with air at that pressure. The temperature at which pure ice would be in equilibrium with pure water at 1 atm. is $+0.0023^{\circ}$, which is regarded elsewhere in this book as simply 0° .

In the case of water, at least five kinds of ice, differing in crystalline form, are known. The four unfamiliar varieties are observed only at high pressures; one of them can be formed from the liquid above 70°C. Only three of the seven phases can, however, exist together at one time in equilibrium, as the phase rule shows.

It happens sometimes that two solid phases of a pure substance can exist in equilibrium along a line on a temperature-pressure diagram. If at any pressure the temperature is raised or lowered away from the temperature at which there is equilibrium, one solid phase will be transformed into the other. This temperature, at which there is equilibrium at a definite pressure, is called the transition point, and the line on the diagram is called the transition curve. These terms are also used under certain circumstances when there is more than one component.

27. The Clapeyron Equation.—This is an exact differential equation which gives the relation between variations of pressure dp and variations of temperature dT for any univariant system, that is, a system whose variance is one. It is also called the Clausius-Clapeyron equation. It is

$$dp/dT = L/T\Delta V, \quad (1)$$

where T is the absolute temperature, p the corresponding pressure, and ΔV is the volume increase of the system of phases when the quantity of heat L is absorbed at the constant temperature T and the constant pressure p . In numerical calculations L would be expressed in mechanical units to correspond to the units of pressure and volume.¹

A system of one component is univariant when there are two phases in equilibrium. There is then a line on the p — T diagram representing the equilibrium between these two phases, and dp/dT is the slope of the line at any point p, T . When the quantity of heat L is absorbed by such a system, a portion of one phase will be converted into the other; for example, a gram of liquid may be converted into vapor, or a gram of ice may be converted into vapor or liquid. In any case, ΔV is the corresponding increase in volume when the same quantity of material

¹ By the use of a conversion factor such as 41.303 cc.-atm. per 15°-cal.

changes in phase. For example, it may be the volume of a gram of vapor minus the volume of a gram of liquid.

The equation explains why the line OB of Fig. 13 slopes upwards to the left in the case of the diagram for H_2O . This slope makes T decrease when p increases; that is, dp/dT is negative. Applying Eq. (1) to the equilibrium between liquid water and ice, L is the heat of fusion and is positive, and ΔV is the volume increase when a gram of ice melts, and this is negative. The absolute temperature T is always positive, and therefore dp/dT must be negative.

Problem

Formulate a definition of critical pressure analogous to the familiar definition of critical temperature, beginning "The critical pressure is the highest pressure at which . . ."

CHAPTER VI

RELATIONS OF GASES TO LIQUIDS OR SOLIDS WHEN ONE OR MORE OF THE PHASES IS A SOLUTION

28. The Gas Phase Is a Solution.—If a volatile liquid be poured into a bottle, partly filling it, and the bottle be stoppered and shaken, a pressure is developed which may drive out the stopper. The liquid evaporates into the air contained in the bottle to about the same extent as it would into the space occupied by the air if this space were empty. Careful experiments show that the concentration of the vapor of the liquid in moles per liter (n_1/V) is very nearly the same whether the volume V is empty originally, or whether it contains a gas.

We suppose here that the gas does not dissolve in the liquid to any considerable extent; if it does, a correction will be necessary, as will be discussed later.

Let us apply the simple gas laws. First consider the liquid shaken with an empty volume V ; let n_1 moles evaporate.¹ The pressure that would be produced by the n_1 moles of vapor alone in the volume V , which pressure we shall call p_1 , is the vapor pressure and will be given by the equation

$$p_1 = RTn_1/V. \quad (1)$$

Consider now the liquid shaken with air. We may in such cases treat the air as if it were a pure gas whose molecular weight is 29. Let n_2 be the number of moles of air in the volume V . According to experiment, the number of moles of liquid which evaporate is again n_1 , the same as before. The total pressure due to n_1 and n_2 will be given by

$$p = \frac{RT}{V}(n_1 + n_2). \quad (2)$$

¹ Computed from the number of grams by the use of the molecular weight of the *gas*.

Comparison of the two equations shows that

$$p_1 = p \frac{n_1}{n_1 + n_2} \quad (3a)$$

or

$$p_1 = px_1, \quad (3b)$$

where x_1 is written for the fraction, called the mole fraction of substance 1.

The above relations hold, no matter how many kinds of gas are present in the mixture, provided we replace the expression $(n_1 + n_2)$ by $(n_1 + n_2 + n_3 + \dots)$, which continued sum of all the mole numbers is usually denoted by Σn (sigma n). The mole fraction x_1 equals then $n_1/\Sigma n$ and we find that the vapor pressure p_1 equals RTn_1/V and px_1 .

In Chap. II, Eq. (9), we found that the total pressure equals the sum of the "partial pressures" RTn_1/V , RTn_2/V , etc. In terms of the simple theory of gases the partial pressure may be taken to designate any of the quantities p_1 , RTn_1/V , px_1 , and the pressure that would be developed by n_1 moles in the volume V of the mixture, since all four quantities are equal according to the simple theory.

The most generally useful of the above equations is Eq. (3b). It was derived by combining with the simple theory of gases the proposition that the number of moles of liquid that evaporate into V cc. of the gas mixture equals the number that evaporate into V cc. of empty space. This proposition appears from the evidence so far collected to be somewhat more accurate than the simple theory of gases itself, consequently Eq. (3b) may be trusted to give results of the same degree of accuracy as the simple theory of gases.

At the high pressures frequently encountered in the physico-chemical laboratory or in industrial plants, Eq. (3), like the simple theory of gases, is quite erroneous. It is, however, a problem for the specialist to determine the extent of the error, and he often uses Eq. (3) as a guide when unable to determine its error.

The biologist should note that the four quantities, mentioned above as being equal according to the simple theory, and often indiscriminately called partial pressure, are not equal at high

pressures. The expression partial pressure connotes low pressure, and is ambiguous when high pressures are under discussion.

29. The Vapor Pressure of a Liquid as a Property of the Liquid Itself.—We may define the vapor pressure of a liquid in such a way as to include the definition given in Chap. V and to extend it to make it more generally useful.

We shall again use the idea of a semipermeable membrane, as in Chap. II. But now, instead of trying to convince ourselves that the kind of membrane we need might theoretically be constructed, let us meet the situation by adopting, once for all, the belief of the men who devise new theoretical proofs, that it is always justifiable to assume the existence of any kind

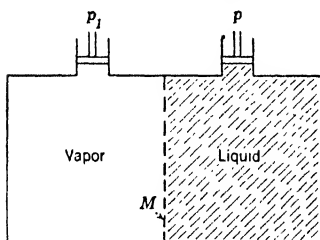


FIG. 14.—Vapor pressure p_1 of a liquid under a pressure p greater than p_1 .

of membrane we please and to use it together with any imaginary mechanisms we please for the purpose of bringing about changes of state.¹

Let us imagine that M in Fig. 14 is a membrane separating a liquid from its vapor at some constant temperature. The membrane is such as to prevent leakage of liquid itself, even under a difference of pressure, but it permits the diffusion of the molecules of the substance in either direction. If the pressure of the vapor be made low enough, by pulling out the left-hand piston, liquid will evaporate through the membrane until the pressure is increased sufficiently; if the pressure of the vapor be too greatly increased, no liquid need be formed in the left-hand compartment, if this is free from dust, but molecules will pass the membrane and be retained as liquid in the right-hand compartment.

Let p_1 be the pressure on the vapor when it is in equilibrium through the membrane with the liquid under the pressure p . Then the vapor pressure of the liquid under the pressure p is defined to be the pressure p_1 . It is easy to show that this defini-

¹ Gibbs even considered purely imaginary *changes of state* ("Scientific Papers," Vol. 1, p. 60, lines 17–19), but we shall not have to do more than to consider real changes of state brought about by imaginary tools.

tion agrees with the original definition when the pressure on the liquid p is equal to that on the vapor p_1 .

To show this, imagine that the pressures p_1 and p are adjusted until we have the condition indicated in Fig. 15. Here the vapor B is supposed to be in equilibrium with the liquid, so that p is the vapor pressure according to the original definition. The vapor A is also supposed to be in equilibrium with the liquid, through the membrane, so that p_1 is the vapor pressure of the liquid under the pressure p , according to the extended definition. But the pressure p_1 of the vapor A must be equal to the pressure p of the vapor B . For suppose they might differ, p_1 for instance being greater than p , when the liquid is in equilibrium with both vapors.

Consider both pistons now fixed in position. Then gas would pass through the membrane from A to B , some of vapor B must condense and, since chamber A has lost in substance and in pressure, liquid must evaporate through the membrane into A . The condition is in no way relieved, and substance must circulate continuously. This is,

however, impossible. If there were in fact any tendency toward such a circulation we could insert a turbine or windmill at a suitable spot and gain a certain amount of mechanical work out of a device which works in cycles. The work would have to come out of nothing at all, or out of the heat of the surroundings. These surroundings we have been tacitly assuming to consist of a constant temperature bath. But the first law of thermodynamics denies that work (or heat) can be produced out of nothing and the second law of thermodynamics denies that work can be produced at the expense solely of the heat of a single reservoir of heat.¹

The laws of thermodynamics show therefore that two vapors in equilibrium with the same liquid must be in equilibrium with each

¹ All actual and all theoretical heat engines producing work take in a certain amount of heat at a high temperature and, to complete their cycles of operation, reject a smaller amount of heat to some second reservoir at a lower temperature.

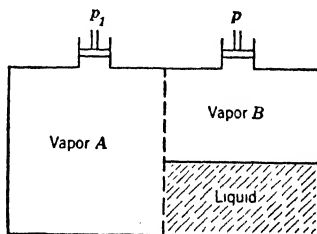


FIG. 15.—Vapor pressure p_1 of a liquid under a pressure p equal to p_1 .

other. The extended definition of vapor pressure includes the one originally given as a special case.

Similar considerations show that whenever two phases are in equilibrium at a given temperature with a third they must be in equilibrium with each other. The phases may be of any kind. We must note however that if two phases are in equilibrium with a third merely with respect to a certain type of transfer of substance, then they need be mutually in equilibrium only with respect to that type of transfer. Thus a solution of sulphuric acid and one of sodium chloride may, if their concentrations are suitable, be in equilibrium with the same mixture of air and water vapor, as respects the evaporation of water. They must therefore be in equilibrium with each other with respect to transfer of water vapor if separated by a membrane permeable to water only. If they are, however, separated by a membrane permeable to sulphuric acid, or if they are brought directly into contact as two layers of liquid, they will not be in equilibrium.

These considerations thoroughly justify the conception of the vapor pressure of a liquid as a property of the liquid itself.¹ For pure liquids the vapor pressure, so conceived, depends both on the temperature and the pressure, for solutions it depends also on the composition. In the case of solutions of more than one volatile component we sometimes speak of the partial vapor pressure of substance 1 in the solution. This is the pressure of pure vapor of substance 1 when the vapor is in equilibrium with the liquid through a semipermeable membrane which passes substance 1 only.

Exactly similar considerations furnish also the justification, promised in Chap. II, for regarding the equilibrium pressure of a single gas in a mixture as a property of the mixture.

30. The Effect of Pressure on Vapor Pressure.—The effect of increasing the pressure on a pure liquid is always to increase its vapor pressure. The truth of this will be seen from a brief consideration of Fig. 16. The tube which contains the liquid

¹ Because we have seen that the value of the vapor pressure does not depend on the nature of the phase with which the liquid happens to be in equilibrium. It is different with surface tension, the value of which for a solution depends on the nature of the phase with which the solution is in contact.

is made of a membrane M , similar to that in Figs. 14 and 15. We now suppose this tube long enough so that the gravitational field of the earth has an appreciable effect on the density of the gas at different levels and a similar, though much smaller, effect on the density of the liquid. Let the crosses indicate points in the liquid and in the vapor at the same level, which is at a distance of l cm. below the free surface of the liquid. Let the density of the vapor at this level be d_1 , and of the liquid, d . Let the pressure of the vapor at this level be p_1 , and of the liquid, p . Then p_1 is the vapor pressure of the liquid under the pressure p . It is clear at once that both pressures will be greater at lower levels, owing to the weights of the columns of the vapor and liquid. A simple application of the calculus gives us a formula for the effect. Consider the effect on the pressure of increasing the distance l by a very small amount dl . The increase in the pressure of the vapor will be $d_1 g dl$, and of the liquid, $d g dl$.¹ The increase in vapor pressure dp_1 produced per unit increase of pressure is dp_1/dp where dp is the increase in the pressure of the liquid corresponding to the increase of vapor pressure. It is evident that

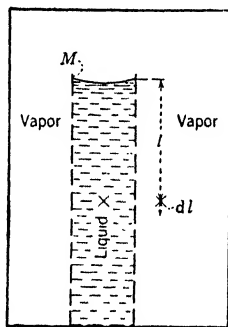


FIG. 16.—Effect of pressure on vapor pressure.

$$dp_1/dp = d_1 g dl / d g dl = d_1 / d. \quad (4)$$

The ratio of the corresponding increases in the two pressures equals the corresponding ratio of the densities (in the limiting case when the differentials approach zero).

If v_1 and v represent the volume of a mole of substance in the vapor state and in the liquid state, respectively, (the molecular weight being considered the same in the liquid as in the vapor state), then $d_1/d = v/v_1$ and hence

$$v_1 dp_1 = v dp. \quad (5)$$

¹ The student unfamiliar with the calculus must not take the d in dl to indicate density or any other quantity. It indicates a very small difference in l .

This can be integrated at once by assuming that the liquid is practically incompressible, so that v is a constant, and that the vapor follows the ideal gas law: $p_1 v_1 = RT$. The temperature is supposed constant. We obtain first

$$RT dp_1 / p_1 = v dp, \quad (6)$$

which gives, on integration between limits,

$$RT \ln \frac{p_1'}{p_1} = v(p' - p), \quad (7)$$

where p_1 is the vapor pressure when the pressure on the liquid is p , and p_1' is the vapor pressure when the pressure on the liquid is p' . When logarithms are obtained by integration (of dx/x), they are "natural" logarithms to the base e , and are denoted throughout this book by \ln . The common logarithm to the base 10 is denoted by \log , and $\log x = 0.4343 \ln x$. Equation (7) furnishes a useful equation for calculating the vapor pressure when the liquid is under any given pressure p , from the *normal* vapor pressure p_{10} , that is, the vapor pressure when the liquid is under the same pressure p_{10} as the vapor.¹ This equation is

$$\log p_1 = \log p_{10} + 0.4343 \frac{v}{RT} (p - p_{10}). \quad (8)$$

In using this equation we may take the volume of the liquid v in cubic centimeters per mole and the pressures in atmospheres if we take R as 82.06 (see Chap. II, page 14).

We shall later make use of Eq. (7) in discussing osmotic pressure.

31. The Effect of Pressure on the Vapor Pressure of a Solution.—The vapor pressure of any constituent of any solution is always less than that of the constituent when pure at the temperature and pressure of the solution. Its value will ordinarily be increased by increasing the pressure on the solution.

We may imagine that a solution of a non-volatile solute in a volatile solvent, such as cane sugar in water, is placed in the apparatus represented by Fig. 16. Or a solution containing

¹ The subscript is one-zero, not ten. The subscript zero is added to indicate a point of reference, somewhat as in "zero hour."

alcohol in water may be placed therein, in which case we may suppose the membrane permeable to but one substance, say water, and may suppose the tube to be closed at the top by a cap made of this semipermeable material. In either case the vapor will be that of pure water, and its pressure at any level will be the vapor pressure of the liquid under the pressure at the given level and at the concentration at the given level. The vapor pressure depends on the concentration, and the concentration of a solution under the influence of gravity depends, though but slightly, on the height, since the heavier molecules tend to accumulate in the lower levels. The variation dp_1 of Eq. (5) is therefore due to a joint action of pressure and composition effects, and the further mathematical operations leading to Eqs. (7) and (8) apply only approximately to the vapor pressure of a solution.

When the pressure is applied by a piston upon a solution of constant concentration, instead of by a gravitational field, the result obtained from the methods of thermodynamics is for solutions similar throughout to that given above for pure liquids, except that v is everywhere replaced by a "partial molal volume" of the solvent in the solution. This partial molal volume is not a quantity which we can represent by a physical picture, but is simply the slope of a curve obtained from density measurements by plotting the volume of a solution containing fixed amounts of substances other than 1 and variable

amounts of substance 1, the temperature and pressure being constant. The volume is plotted as the ordinate, and the amount of substance 1 as abscissa, as in Fig. 17.

When a physical chemist speaks of the effect of pressure on vapor pressure, he thinks of the pressure as being applied by a piston and uses the equations given in the preceding section, after replacing the molal volume of the solvent with the partial molal volume of the solvent in the solution, when this is necessary. When the solution is very dilute he does not need to make this

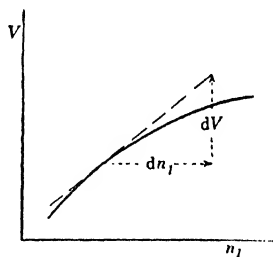


FIG. 17.—The partial molal volume dV/dn_1 , the following quantities being held constant: T , p , and numbers of moles of all substances other than of kind 1.

substitution, as the partial molal volume is nearly equal to the molal volume of the pure solvent for a dilute solution, the equality becoming exact as the solution is infinitely diluted and the concentration approaches zero.

We shall accordingly use Eq. (7) as it stands when discussing the osmotic pressure of dilute solutions.

The vapor pressure of any constituent of a solution is practically always increased when the pressure on the solution is increased.¹

32. Both Gas and Liquid Phases Are Solutions.²—For the consideration of this case we need no new principles. We shall use as good approximations the following rules: (1) See Fig. 18.

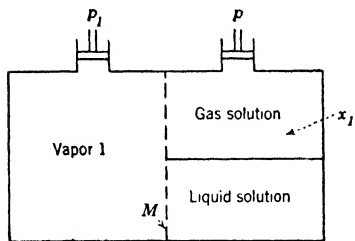


FIG. 18.—Partial vapor pressure p_1 of a liquid solution.

The partial vapor pressure p_1 , being equal to the equilibrium pressure of the gas 1 in the gas solution, is practically equal to the product px_1 , where x_1 is the mole fraction of substance 1 in the gas solution, whose pressure is p (Chap. II). (2) The partial vapor pressure p_1 is practically the same, whether the pressure on the liquid mixture is

p_1 , or the total vapor pressure p , or even 1 atm. Its value may often be calculated from Raoult's law, as explained in Chap. VIII.

These rules are used in gas analysis to calculate how much dry gas is present in a volume of gas saturated with moisture from a film of pure water (or from a solution of known concentration and vapor pressure). Permanent gases do not dissolve in water at the pressures employed enough to change the vapor pressure of the water to a significant extent. Let p_1 be the vapor pressure of the water, and p be the pressure of the moist gas. Then

¹ In the curious case that the partial molal volume of a constituent in a solution is negative, the effect of pressure would be opposite. This case is rare, and there is very likely a chemical reaction when such a constituent is added to the solution, so that we might well be cautious with regard to the question: what are the constituents of the solution?

² We do not distinguish between the words mixture and solution when speaking of gases, as every gas mixture is necessarily a solution.

$p_1 = px_1$, where x_1 is the mole fraction of water in the moist gas. By subtracting the vapor pressure p_1 from the total pressure p we obtain according to these rules

$$p - p_1 = p - px_1 = p(1 - x_1). \quad (9)$$

Now according to the simple theory of gas mixtures (Chap. II, page 18),

$$P = \frac{RT}{V}(n_1 + n_2 + n_3 + \text{etc.}) = \frac{RT}{V}\Sigma n, \quad (10)$$

and

$$1 - x_1 = 1 - \frac{n_1}{\Sigma n} = \frac{\Sigma n - n_1}{\Sigma n}. \quad (11)$$

Hence,

$$p - p_1 = p(1 - x_1) = \frac{RT}{V}\Sigma n \times \frac{\Sigma n - n_1}{\Sigma n} = \frac{RT}{V}(\Sigma n - n_1). \quad (12)$$

The total pressure thus corrected for the vapor pressure by subtraction of the vapor pressure is therefore equal to the pressure that would be exerted by the molecules other than those of kind 1 in the volume V and at the temperature T of the mixture. Solving for the number of these moles, we have

$$\Sigma n - n_1 = (p - p_1)\frac{V}{RT}. \quad (13)$$

Hence the volume which these moles (of dry gas) would occupy at the standard temperature T_0 and pressure p_0 (zero Centigrade and 1 atm.) is given by

$$V_0 = \frac{RT_0(\Sigma n - n_1)}{p_0} = \frac{RT_0(p - p_1)V}{p_0RT} = \frac{(p - p_1)T_0V}{p_0T}. \quad (14)$$

The measured volume V is thus simply corrected by appropriate multiplication and division by the pressure and temperature ratios, after the subtraction. If $(p - p_1)$ is given in millimeters of mercury (at zero degrees and at the standard value of gravity) then p_0 is 760; if it is given in atmospheres, p_0 is 1. The temperatures T and T_0 are of course absolute. V_0 comes out in whatever units were used to measure V .

Problems

1. Calculate the volume that would be occupied under standard conditions by the dry gas in a gas mixture which occupies at 25°C. , when saturated with pure water, 40 cc. at 735 mm. of ice-cold mercury. Consult a handbook.
2. Show that the vapor pressure of ice must equal that of water when the ice is in equilibrium with the water and each phase is under a pressure equal to its vapor pressure, and at the same temperature. Use the laws of thermodynamics.

CHAPTER VII

THE MEASUREMENT OF VAPOR PRESSURE. STEAM DISTILLATION

33. Methods of Measurement.—There are two general methods of measuring vapor pressure: the direct, and the gas-bubbling method. The direct method is applicable to pure liquids or to liquid solutions from which only one constituent is volatile. In the static method the pressure of the pure gas is directly measured after the gas has been brought to equilibrium with the liquid by stirring, and is thus a direct application of the definition of vapor pressure. In the dynamic method the pressure is found that is just sufficient to prevent boiling of the liquid. These two subdivisions do not therefore differ in principle, but merely in the technique. In either method the temperature must be controlled and especial care must be taken to ensure the absence of air or other undesired gases from the space above the liquid.

In the gas-bubbling method, air or some other inert gas is bubbled through the liquid, thus permitting the liquid to evaporate into the air bubbles. The bubbles expand. If they are well exposed to the liquid before they escape from it they should come to equilibrium with it, and the vapor pressure of the liquid may be estimated by analyzing the contents of the bubbles.

One way of doing this is to determine the volume of air plus substance that comes out of the apparatus, either experimentally, or by adding the computed volume (usually small) of the substance as a gas to the measured volume of pure air (after removal of the substance). Let this total volume be V . We must also determine how many moles n_1 of substance were evaporated, which may be done by condensing the vapor in a freezing mixture, or by absorption in a weighed amount of an absorbent. The simple laws of gases and of gas mixtures are now usually applied.

The pressure that the pure gas would have, if n_1 moles were in the total volume V , is RTn_1/V . This equals therefore the vapor pressure, since the number of moles that evaporate into a gas is taken equal to the number that would evaporate into the same volume V if originally empty (see Chap. VI, page 46). Another way, nearly the same, is to determine by any suitable method how many moles n_2 of air passed through the apparatus, and how many moles of substance n_1 . Then the mole fraction of substance in the volume V , regarded as a very large gas phase in equilibrium with the liquid phase, is readily calculated¹ and the vapor pressure is taken equal to the product px_1 , where p is the pressure at which the air was bubbled through the liquid.

However this is managed, the air-bubbling method is not so accurate in principle as the direct method, because of the use of approximate equations of state, and the error may possibly reach 1 per cent. Since we seldom have the necessary semipermeable membranes, the direct method itself cannot usually be applied to solutions containing more than one volatile constituent without the use of some approximate relation.

34. Steam Distillation.—When a liquid, such as aniline, is not completely miscible with water in the neighborhood of the boiling point of water, so that two layers of liquid are formed, the liquid may be steam distilled by passing steam through it and condensing the mixed vapors. By means of a separatory funnel the aniline layer of the distillate may be freed from the water layer and subsequently dried in some manner. In practice, steam distillation is used to purify the liquid, so that the temperature of the distillation may change because of changes of composition of the residual liquid layers in the distillation flask. When there are only two components, as pure aniline and water, the temperature is fixed, according to the phase rule, by the prevailing pressure, and will not depend on the relative masses of the two liquid layers.

Consider a volume V of vapor from the flask before it is condensed. Let it contain n_1 moles of the aniline and n_2 moles of water; let the partial vapor pressure of the aniline be p_1 and

¹ $x_1 = n_1/(n_1 + n_2)$.

that of the water be p_2 . Then according to the simple theory of gases we have

$$p_1 = n_1 \frac{RT}{V}$$

or
$$n_1 = p_1 \frac{V}{RT}. \quad (1)$$

Similarly,
$$n_2 = p_2 \frac{V}{RT}. \quad (2)$$

Hence,
$$n_1/n_2 = p_1/p_2. \quad (3)$$

The number of moles that distill is proportional to the vapor pressure. Now, the method is generally used for high boiling liquids, which have then a lower vapor pressure than water, so that fewer moles of the liquid pass over than of water. The relation in terms of the numbers of grams of liquid that pass over is more favorable. When n_1 moles pass over, the number of grams m_1 distilled is $n_1 M_1$, where M_1 is the molecular weight. We have then

$$m_1 = n_1 M_1 = M_1 p_1 \frac{V}{RT}$$

and
$$m_2 = M_2 p_2 \frac{V}{RT}; \quad (4)$$

from which
$$\frac{m_1}{m_2} = \frac{M_1 p_1}{M_2 p_2}. \quad (5)$$

The high boiling liquids usually have high molecular weights, whereas water has an exceptionally low molecular weight of 18, and hence the number of grams of liquid that come over per gram of water, m_1/m_2 , is often sufficient to make the method practicable, even when the vapor pressure of the high boiling liquid is quite low in comparison with that of water at the boiling point of the mixture, which is ordinarily a few degrees below the boiling point of pure water.

If the two liquids are practically insoluble in one another at the boiling point, Eq. (5) can be used to calculate the yield from

the vapor pressures of the pure liquids, because the vapor pressure of a liquid is not affected by the mere presence of another beside it. If, however, the two liquids dissolve in each other to a certain extent, we must put into Eq. (5) the actual values of the partial vapor pressures of the two constituents as existing in the solutions. These may, in case of need, be estimated by the use of Raoult's law, which is explained in the next chapter.

Problems

1. Why is the boiling point of two volatile immiscible liquids lower than that of either of the pure liquids?
2. Consider two partially miscible volatile liquids in equilibrium with their vapor. Each of the two liquid phases has two constituents and two corresponding (and different) partial vapor pressures. How many different partial vapor pressures does this make, and why?

CHAPTER VIII

THE VAPOR PRESSURE OF LIQUID SOLUTIONS

There are a few pairs of liquids which mix to form solutions of which the partial vapor pressures can be computed, for all percentages, by a remarkably simple law, called Raoult's law.

35. Raoult's Law.—Let us use here x_1 and x_2 to denote the mole fractions of the two components of such a solution.¹ Then if p_{01} represents the vapor pressure of pure substance 1 at the given temperature, the law states that the vapor pressure p_1 of substance 1 in the mixture at this temperature is proportional to the mole fraction x_1 , or

$$p_1 = kx_1. \quad (1)$$

But k must here equal p_{01} , for when x_1 happens to be equal to 1, the liquid consists of pure substance 1, and the vapor pressure p_1 equals p_{01} in accordance with the definition of p_{01} and at the same time p_1 equals k in accordance with Eq. (1). Raoult's law is therefore expressed by the equations

$$p_1 = p_{01}x_1, \quad (2)$$

$$p_2 = p_{02}x_2, \quad (3)$$

where p_{02} is the vapor pressure of pure liquid 2. The total vapor pressure due to both constituents will be approximately

$$p = p_1 + p_2 = p_{01}x_1 + p_{02}x_2, \quad (4)$$

$$p = p_{01}x_1 + p_{02}(1 - x_1),$$

$$p = (p_{01} - p_{02})x_1 + p_{02}. \quad (5)$$

Hence if the total pressure be plotted against x_1 we shall obtain a straight line. If p_1 be plotted against x_1 , and p_2 against x_2 , we must, from Eqs. (2) and (3), obtain also straight lines. In

¹ Observe that x_1 and x_2 refer now to the composition of the liquid, instead of the gas, as hitherto.

Fig. 19 these three lines are plotted. The two partial vapor pressures, p_1 and p_2 , are given by light lines; the total pressure, by the heavy line. The broken line can be used, if desired, to show that the heavy line is the plot of Eq. (5).

In order for Raoult's law to hold exactly *for every solution* of two given liquids, from 0 to 100 mole per cent, the two liquids must be extremely similar. Similarity may be judged in part by absence of volume changes or of heat effects on mixing the liquids. Benzene and toluene are very similar, and the vapor pressure lines are nearly as straight as in Fig. 19.

But in order for Raoult's law to hold merely *for some solutions*

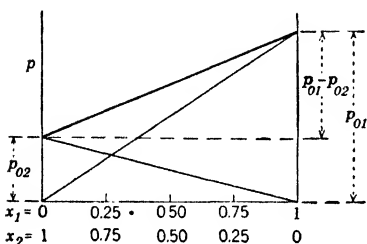


Fig. 19.—Vapor pressure lines according to Raoult's law.

of two given liquids it is not necessary that the two substances be at all similar, or even that they both be liquids. There is a vast number of pairs of substances for which $p_1 = p_{01}x_1$ when x_1 is nearly unity, the subscript 1 representing either constituent. We say that Raoult's law holds for the solvent in a dilute solution,

distinguishing solvent and dissolved substance (solute) merely for convenience, calling either substance solvent when it is present in considerable excess. And we adopt as a fundamental law of the dilute solution that Raoult's law holds for the solvent in it.

The mole fraction is computed from weighed quantities of liquid or solid by the use of the same molecular weights which the substances have in the gaseous state. As a matter of fact, when Raoult's law does not hold for dilute solutions, using these molecular weights, it has always been found possible to find a reasonable value for the molecular weight of the solute which makes the law correct. This is notably the case for salts and other substances which in water are believed to be dissociated.

The shrewd reader will notice that when x_1 is unity p_1 is necessarily equal to $p_{01}x_1$ as a mathematical matter, having nothing to do with experiments. When we say that in many cases $p_1 = p_{01}x_1$ when x_1 is unity, we mean something more than the circumstance that the partial vapor pressure line must cut the axis of

coordinates representing 100 per cent of substance 1 at the pressure p_{01} . We mean, besides this, that the partial vapor pressure line has, near this axis, *the same slope* as the straight line defined by the equation $p_1 = p_{01}x_1$. This is illustrated in Fig. 20. The light curved lines show the partial vapor pressures of acetone and carbon disulphide for various mixtures of these two liquids, as experimentally determined at a constant temperature of 35.17°C.¹ The broken straight lines show what the partial vapor pressures would be according to Raoult's law. Extreme deviations from Raoult's law are shown, but the partial vapor pressure lines curve in closer and closer to the Raoult's law lines, and each of them has at one end the same slope as required by Raoult's law. This curving in and this agreement of slope occur in each case only toward the end of the line that represents 100 per cent of the component in question. The heavy curved line gives the total vapor pressure corresponding to any given mole percentage of one of the liquids. The curved broken line gives the total vapor pressure corresponding to any given mole fraction of a constituent in the vapor; all the other lines are drawn with reference to the mole fraction in the liquid.

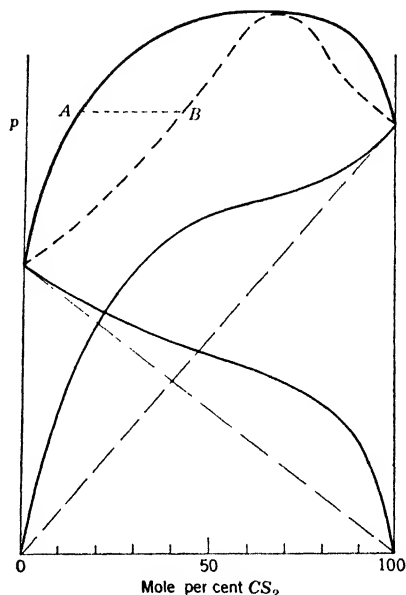


FIG. 20.—Vapor pressures of acetone-carbon disulphide mixtures.

The liquid composition-total pressure line (heavy curve in Fig. 20) and the vapor composition-total pressure line (broken curve) are of great importance in the theory of distillation. If a horizontal line (dotted in Fig. 20) be drawn so as to intersect these two lines in two points such as A and B, the compositions

¹ ZAWIDSKI, *Z. physik. Chem.*, **35**, 129 (1900).

corresponding to these points belong to a liquid *A* and a vapor *B* which are at the same experimental temperature and at the same pressure (because the line *AB* is horizontal). The compositions *A* and *B* are in fact the compositions of the liquid and the vapor when they are in equilibrium; this being the basis on which such curves are drawn.

It will be observed that the vapor composition line touches the liquid composition line at the highest point of the latter, at about 67 mole per cent of carbon disulphide. When a liquid of this composition is distilled at 35.17° (by properly adjusting the pressure upon it), the composition of the vapor is the same as that of the liquid; hence the composition of the liquid does not change during the distillation, and its vapor pressure is therefore constant during the distillation.

In the case of aqueous solutions it is found that in dilute solutions Raoult's law may be used to calculate the vapor pressure of the water, provided the dissolved substance is not an electrolyte. This important exception gives rise to a separate chapter in physical chemistry, and will be discussed later.

36. Constant Boiling Mixtures.—In the case of acetone and carbon disulphide the total vapor pressure curve reaches a maximum, and at this point the compositions of the liquid and of the vapor in equilibrium with it are the same. Now the boiling point is merely the temperature at which the liquid and the vapor are in equilibrium at a given pressure, usually at 1 atm. Of two solutions, the one with the greater vapor pressure has evidently the lower boiling point. In accord with this, two substances which show a maximum in the vapor pressure curve show a minimum in the boiling point curve obtained by plotting the boiling point against the mole fractions. The curves are similar to those of Fig. 20, but the vapor composition line lies above the liquid composition line except at their lowest point, where they touch. At this point, since both phases have the same composition, the liquid can be distilled at constant pressure, constant composition, and constant temperature.

Constant boiling mixtures were at one time believed to be chemical compounds of the two substances. It was shown, however, by experiment that the composition of the constant boiling mixture depends, even though slightly, on the pressure

at which distillation takes place. Gibbs showed also that whenever it happens that the composition of the vapor is the same as that of the liquid the pressure or the temperature will be a maximum or a minimum.

Ethyl alcohol and water form a constant (minimum) boiling mixture which is the 95 per cent alcohol of commerce. Because the boiling point of this mixture is less than that of any other it is impossible to separate 100 per cent alcohol from this mixture by distillation alone, or to get a stronger solution than this from a weak solution, or to get a weaker one than this from a stronger one. Solutions of water and alcohol can be separated by fractional distillation into water and 95 per cent alcohol, or into 100 and 95 per cent alcohol, according to the original strength. Methyl alcohol and water do not form a constant boiling mixture, and anhydrous methyl alcohol can be prepared by rectification of weak solutions and has been much used for dehydrating biological preparations.

Hydrochloric acid and water form a constant, maximum, boiling mixture, as does water with each of the following strong acids: hydrofluoric, perchloric, hydrobromic, hydriodic, nitric, and formic.

When constant boiling alcohol (minimum boiling point) is to be prepared by distillation, it is the distillate whose composition is more nearly that of the constant boiling mixture and indeed the first portion of the distillate. When constant boiling hydrochloric acid (maximum boiling point) is to be prepared, as for standardizing volumetric solutions¹, it is the residue in the distilling flask whose composition is more nearly that of the constant boiling mixture and indeed the last portions of the residue.²

Whenever a diagram is at hand giving the vapor and liquid composition curves, the composition of the first portion of distillate from any solution can be immediately determined from the diagram by drawing a line such as *AB* of Fig. 20 and noting the composition of the vapor which corresponds to the given composition of the liquid. By the use of this principle the diagram can be applied to explain the complete course of the

¹ Method of Hulett and Bonner. See FOULK and HOLLINGSWORTH, *J. Amer. Chem. Soc.*, **45**, 1220 (1923).

² Provided, of course, the water and acid are free from impurities.

distillation, and indeed whether there is a maximum or a minimum or neither.

Constant boiling mixtures have lately been called azeotropic mixtures, and are so indexed in "International Critical Tables."

They are sometimes formed during the distillation of solutions containing more than two constituents. Ethyl alcohol, water, and benzene form an azeotropic mixture which boils lower and contains more water than ordinary 95 per cent alcohol. A process has been worked out for utilizing this fact in the preparation of absolute alcohol by distillation.

37. Henry's Law.—Consider the vapor pressure of carbon dioxide from a dilute solution in water. Raoult's law may be applied to the vapor pressure of the water, but not to the vapor pressure of the carbon dioxide, as this would imply that Raoult's law holds over the whole range of composition. This is unlikely, as water and carbon dioxide are hardly similar substances. In such a case, provided the substance does not react to too great an extent with the water, we can apply Henry's law. This states, in a familiar form, that the amount of gas dissolved at constant temperature by 1 cc. of a liquid is proportional to the pressure of the gas, or to the partial pressure of the gas in a gas mixture.

We prefer a reversed form of the law, as follows: the vapor pressure of the substance in a dilute solution is proportional to the mole fraction of the substance in the solution. Henry's law for the dissolved substance holds when its mole fraction is small. It may be written

$$p_1 = kx_1 \text{ (when } x_1 \text{ is small).} \quad (6)$$

Compare this with Raoult's law:

$$p_1 = p_{01}x_1 \text{ (when } x_1 \text{ is nearly unity),} \quad (7)$$

which applies to substance 1, if it is in excess, like the water in the carbon dioxide solution, provided there is not too much chemical action between solvent and solute. The similarity is great. The difference is that Eq. (7) holds when x_1 is, in the limit, equal to 1, so that the proportionality constant is evidently p_{01} , the vapor pressure of pure liquid 1. In the case of Eq. (6), k does not have to be equal to the vapor pressure of substance 1.

since the equation usually fails except when x_1 is small. As a matter of fact, the proportionality constant k of Henry's law is not related in any known way to the vapor pressure of the pure substance and has to be determined by experiment.

In stating Henry's law, it is often said that the concentration, in moles of dissolved substance per liter, is proportional to the pressure of the gas. Since the law usually holds only when x_1 is small, it usually makes little difference how the amount of dissolved substance is expressed.¹

38. Relation between Raoult's and Henry's Laws.—The relation between Raoult's and Henry's laws can be seen by turning back to Fig. 20. Consideration of either one of the partial vapor pressure lines shows that, when the mole fraction approaches unity, the slope of the line approaches the Raoult's law slope of the straight broken line, but that when the mole fraction approaches zero, the slope of the line is quite different from that of the straight line, although the curved line here becomes nearly straight, practically coinciding with a new straight line of its own. Mathematically, the slope approached in the former case is p_{01} , and in the latter is merely k , a number not known until experiments are made on the mixtures.

There is a very remarkable proof in chemical thermodynamics that Raoult's law holds for the solvent in a dilute solution when Henry's law holds for the solute in the same solution and *vice versa*. It is not necessary to understand by Henry's law that the gently curved line of limiting slope k is really straight, but only that k is neither zero nor infinite, that is, that the curved line does not approach either axis of coordinates asymptotically.

In the rare cases when Raoult's law holds for both constituents over the whole range of composition, the difference between

$$^1 \text{ Proof: } p_1 = \frac{kn_1}{(n_1 + n_2)} = k \frac{n_1}{n_2} \frac{1}{(1 + n_1/n_2)} = k \frac{n_1}{n_2} \left(1 - \frac{n_1}{n_2} + \frac{n_1^2}{n_2^2} - \text{etc.} \right).$$

Hence, when $\frac{n_1}{n_2}$ is small compared with unity, we have approximately $p_1 = k \frac{n_1}{n_2}$, which means that the vapor pressure is proportional to the number of moles n_1 when the number of moles of solvent n_2 is constant. But, so long as the solution remains dilute, the volume of the solution is practically constant when the number of moles of solvent is constant. Therefore the vapor pressure p_1 is nearly proportional to the number of moles of solute dissolved in a given constant volume of solution.

Raoult's and Henry's laws totally disappears, as k must then equal the partial pressure of the pure liquid.

39. The Distribution Law.—In the chemical laboratory it often happens that we wish to remove from an aqueous solution some substance which is soluble in ether, or in some other substance which does not mix with water in all proportions. We shall consider ether as a concrete example of such a substance.

This can be done by shaking the solution together with some ether in a separatory funnel, removing the ether solution, and treating the solution repeatedly with ether in this way until nearly all of the substance is removed. The ether can then be evaporated, leaving the substance. If the shaking process is continued each time until equilibrium is reached, and if the solutions in water and in ether are dilute, a remarkably simple law holds throughout the extraction process: the mole fraction of the substance in the ether layer x_e is proportional to its mole fraction in the water layer x_w , or

$$x_e/x_w = k, \quad (8)$$

where the proportionality constant k is the distribution constant.

It is easy to see that the distribution law is a consequence of Henry's law. The two liquids are brought to equilibrium with each other. If one of them were also brought to equilibrium with a vapor phase, the other would be in equilibrium with the same vapor, according to the principle given in Chap. VI, page 50. By Henry's law,

$$p_1 = k_e x_e,$$

and

$$p_1 = k_w x_w, \quad (9)$$

where p_1 is the partial vapor pressure of the substance to be distributed, and k_e and k_w are the Henry's law proportionality constants for ether and water, respectively. Hence we have the distribution law:

$$x_e/x_w = k_w/k_e = k. \quad (10)$$

The constant k in the distribution law is thus the ratio of the Henry's law constants.¹

¹ We may of course write $x_w/x_e = k'$ with equal correctness. If we wish to distinguish, we may call k' the distribution constant *in favor of the water*, and k of Eq. (8) that *in favor of the ether*.

Apparent exceptions to the distribution law for dilute solutions, like those to the law of Raoult or of Henry, have been explained by supposing that the molecular weight of the substance in the liquid state is not the same as in the gas state, or that it differs according to the solvent.

Thus, acetic acid appears to consist of double molecules $(\text{CH}_3\text{COOH})_2$ in benzene solution, but practically of single molecules (CH_3COOH) in water solution.

The distribution law may be regarded as a simple application of the mass action law, to be studied later, and it is not difficult, starting with the mass action law, to modify the distribution law to take care of the case where the substance has two definite and different molecular weights in the two phases.

40. Effect of Temperature.—The proportionality constants of all three laws depend upon the temperature.

CHAPTER IX

VAPOR PRESSURE LOWERING. BOILING POINT ELEVATION. FREEZING POINT DEPRESSION

In this chapter solutions of one non-volatile solute in a volatile solvent are considered.

41. Vapor Pressure Lowering.—Let p_1 be the vapor pressure of the solvent in the solution, and p_{01} its vapor pressure when pure. Then, from Raoult's law,

$$p_1 = p_{01}x_1. \quad (1)$$

But when there are only two components,

$$x_1 + x_2 = 1.$$

Hence,
$$p_1 = p_{01}(1 - x_2). \quad (2)$$

From this we have

$$\frac{p_{01} - p_1}{p_{01}} = x_2. \quad (3)$$

The quantity on the left is called the relative lowering of vapor pressure. If multiplied by 100, it would give the percentage by which the vapor pressure of the solvent has been lowered by dissolving substance 2. The relative lowering equals the mole fraction of the solute, and turns out to be independent of the temperature, since Raoult's law itself holds for different temperatures.

42. Boiling Point.—The boiling point is the temperature at which a liquid is in equilibrium with its vapor at a given pressure. It is usually possible to raise the temperature of a liquid somewhat above its boiling point, whereupon the liquid begins to boil; bubbles form freely and the liquid distills. Some liquids, notably water, can be considerably superheated and then "bump" when they boil, that is, a considerable quantity of liquid explodes into vapor from time to time. The boiling point of a pure liquid

is therefore measured by placing a thermometer in the vapor, rather than in the liquid, and the heating is so conducted that the thermometer bulb is bathed in both vapor and in condensed liquid. The boiling point of a solution may be measured by placing the thermometer in the vapor, provided the thermometer bulb is bathed alternately with vapor and with splashes of solution by means of a special apparatus, similar in action to a coffee percolator.¹ Formerly the thermometer was placed in the solution, and bumping was more or less successfully prevented by the introduction of glass beads and sharp-edged pieces of platinum into the solution, with or without the aid of internal electric heating.

Since the vapor pressure of an aqueous solution of a non-volatile solute at 100° is less than that of pure water, the solution will be below its boiling point when the pressure is 1 atm., and consequently we must raise the temperature above 100° in order to reach the boiling point of the solution.

43. Boiling Point Elevation.—

Figure 21 shows some vapor pressure curves in the neighborhood of the boiling point. Curve AB is the vapor pressure curve of the pure solvent; $A'B'$ is that of a dilute solution; and $A''B''$ that

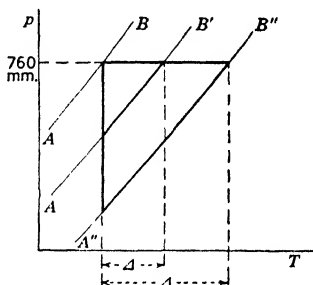


FIG. 21.—Boiling point elevation and vapor pressure.

of a dilute, but a stronger solution. If both solutions are dilute, the curves will be nearly parallel.² The boiling points at 1 atm. are evidently given by the intersections of the curves with the horizontal line at 760 mm. At any given temperature, the vapor pressure of the solution is lower than that of the solvent; and it is evident from the figure that at any given pressure, the boiling point of the solution is higher than that of the solvent. The elevation of boiling point is denoted by Δ (delta). For small values of Δ the vapor pressure

¹ An apparatus has been described by Cottrell, *J. Am. Chem. Soc.*, **41**, 721 (1919).

² This implies that no heat effect takes place when pure solvent is mixed with the dilute solution at the same temperature.

lines are nearly straight, and we may consider the figures in heavy lines as triangles. The vertical sides of the triangles give the lowerings of vapor pressure, and the horizontal sides give the elevations of boiling point. From the properties of similar triangles it is evident that the elevation of boiling point is proportional to the lowering of vapor pressure. Since this equals $p_0 x_2$, Δ is proportional to x_2 , the mole fraction of the solute. (Observe that p_0 is here a constant, equal to 760 mm.) From thermodynamics the proportionality constant can be determined in terms of the heat L required to vaporize a mole of solvent. An approximate equation for the elevation of boiling point is

$$\Delta = \frac{RT^2}{L} x_2. \quad (4)$$

44. Freezing Point Depression.—The freezing point of a dilute solution is the temperature at which the solution is in equilibrium with the pure solid phase of the solvent. It is usually determined at 1 atm. The freezing point under the vapor pressure is the same within a few thousandths of a degree as its value at 1 atm., and the slight difference will be practically the same for dilute solutions as for the pure liquid. We shall therefore consider the freezing points when the pressure is equal to the vapor pressure. In

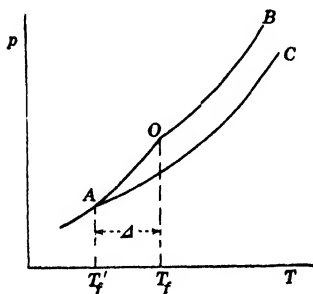


FIG. 22.—Freezing point depression and vapor pressure.

Fig. 22, let OB be the vapor pressure curve of the pure solvent and AO be that of the pure solid phase; then the intersection O will give the freezing point of pure solvent (at T_f), since at this temperature alone will the liquid and solid have the same vapor pressure and hence be in equilibrium with each other.

Let AC be the curve for a dilute solution. Then its intersection A with the curve AO will give the freezing point of the solution (at T'_f), since at this temperature the solution has the same vapor pressure as the solid solvent. Since the vapor pressure of the solution is lower than that of the pure liquid, its freezing point must also be lower. Again, for dilute solutions

proportionality holds between freezing point depression Δ and vapor pressure lowering, and therefore again between Δ and x_2 , the mole fraction of the solute.

Thermodynamics gives an approximate equation for dilute solutions:

$$\Delta = \frac{RT^2}{L_f} x_2, \quad (5)$$

where L_f is the latent heat of fusion of one mole of solid solvent and Δ is the freezing point depression.

In the use of Eqs. (4) and (5) R and L must be in the same units, usually calories per mole. Since R is also *per degree*, it must agree in temperature scale with T . Consistent units are obtained by using Centigrade absolute for T , and the value $R = 1.987$ calories per mole and per degree Centigrade. In calculating the latent heat per mole, the latent heat per gram is multiplied by the molecular weight *in the gas phase*. If the solute is one of those whose molecular weight in solution is abnormal (that is, different from its molecular weight in the gas phase), this abnormal molecular weight must be used in calculating x_2 from the number of grams of substance taken.

45. Determination of Molecular Weights.—The formulas given in the preceding sections for relative lowering of vapor pressure, boiling point elevation, and freezing point depression all presuppose a knowledge of the molecular weights of both solute and solvent, since the mole fraction cannot be calculated from weighed quantities in grams, m_1 , m_2 , etc., without our knowing the corresponding molecular weights, M_1 , M_2 , etc. The molecular weight of the solute must be known for the substance as it exists in the solution, in case it is not the same as in the gas phase. The molecular weight of the solvent can always be taken as the same as in the gas.

The chemist often makes use of approximate formulas derived from Eqs. (3), (4), and (5) to calculate the molecular weight when it is not known, from the effects on vapor pressure, boiling point, or freezing point, produced by dissolving a known weight of solute (2) in a known weight of a suitable solvent (1).¹ For

¹ When the osmotic pressure can be measured, this can also be used to calculate the molecular weight. See Chap. X, Eq. (9).

the best results he must study the effect of the solute when it is in dilute solution.

Instead of using the latent heats in the calculation of the molecular weight from the values of Δ , the chemist usually prefers to measure the effect on the boiling point or freezing point of a known quantity of a substance of known molecular weight, thus determining the value of the constant k in the equation

$$\Delta = \frac{RT^2 n_2}{L(n_1 + n_2)} = (\text{approx.}) \frac{RT^2}{Ln_1} n_2 = kn_2. \quad (6)$$

Here n_2 is the number of moles of solute dissolved in 1,000 grams of solvent. This makes n_1 a constant ($= 1,000/M_1$). RT^2 is nearly constant and therefore also k . The constant k is the ebullioscopic or cryoscopic constant, according as boiling or freezing points are in question. Values of k can be found for the two methods in "International Critical Tables." By use of Eq. (6) the number of moles n_2 dissolved in 1,000 grams of solvent can be calculated from the observed value of Δ , and comparison with the known number of grams dissolved gives the molecular weight.

Any of the effects observed for a given concentration are the smaller, the larger the molecular weight of the solute. When the molecular weight is very large, as is the case with proteins, the effects are very small indeed, and the molecular weight is measurable only with great difficulty. A further difficulty is presented by the impurities of low molecular weight which are likely to be associated with the protein, and thus obscure or quite falsify the results.

A solvent much used of late for substances of high molecular weight is camphor, the cryoscopic constant k of which is unusually high, being 49.8°C. per unit concentration (in moles per kilo of solvent). This is about ten times as large as the constants of the solvents formerly used.

46. Determination of Freezing Points.—If a pure liquid is cooled by exposure to a freezing mixture it often happens that the ice does not immediately form and the temperature will then continue to fall, even below the freezing point. If the

temperature observed in such a case be plotted against the time, a curve like Fig. 23 will be obtained. It is called a cooling curve. Usually at some point such as *A*, crystals will form, or may be induced to form by scratching the inside of the container or by introducing a trace of the ice. As soon as the ice begins to form, the temperature rises to a point such as *B*, and heat is given out by the formation of ice (the latent heat of fusion) so that the temperature remains constant for a time, along the line *BC*, until the liquid is nearly or quite entirely frozen, at the point *C*. On account of the loss of heat to the freezing mixture, the temperature now begins again to fall.

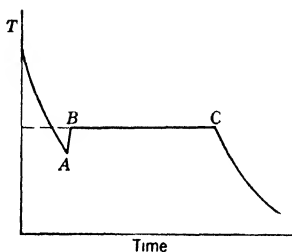


FIG. 23.—Cooling curve of a pure liquid.

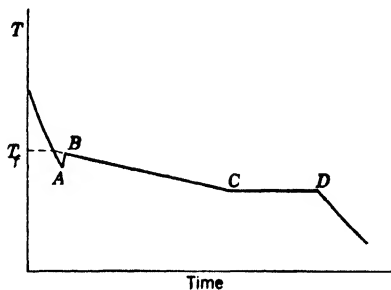


FIG. 24.—Cooling curve of a solution.

Along the line *BC* the liquid and solid would be in equilibrium, if we protected the two phases against the continuous loss of heat, and the corresponding temperature is the freezing point.

It might appear accidental that the heat of solidification is just enough to keep the temperature constant along the line *BC*. The phase rule however requires that the temperature be constant when liquid and solid (of a pure substance) are in equilibrium at a given pressure.

The same thing does not apply to the freezing point of a solution, as this will depend on the composition, and the concentration of a solution will increase as ice is frozen out of it. The cooling curve for a solution will look more like Fig. 24. When, at *A*, the ice begins to form, the temperature rises to *B*, and thereafter falls, though at a smaller rate, until at *C* the solution has become as concentrated as a saturated solution of the dis-

solved substance at the temperature in question. Along the line CD the solution can be in equilibrium with ice and with solid solute. When the solution is quite solid the temperature will again begin to fall. The temperature along CD is called the eutectic temperature. The temperatures along BC are freezing points. The freezing point T_f corresponding to the concentration of the original solution (before any enrichment by separation of ice) may be found by extending BC until it cuts the first portion of the cooling curve. If this temperature differs too much from that corresponding to the point B , the experiment should be repeated with care to prevent so much supercooling.

A more precise way to determine the freezing point of solutions

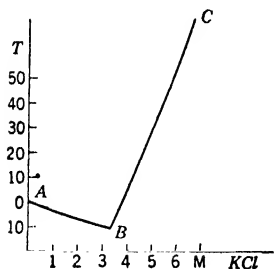


FIG. 25.—Freezing point and solubility curves. The composition is in molality of KCl; *i. e.*, moles KCl per kilo of water.

is to apply the definition of freezing point directly. A thick mixture of solution and pure shaved ice is slowly stirred with care to avoid loss or gain of heat. A thermometer (or thermocouple) is immersed in the mixture. When equilibrium is reached, as judged by the constancy of temperature, some clear solution is removed with a cold pipette and analyzed. This gives the composition corresponding to the freezing point read on the thermometer. After determining the freezing points for a series of solutions of different

strengths, a smooth curve can be plotted showing the freezing point for a desired composition. This curve is a "freezing point-composition curve." The method is essentially the same as that used for determining the solubility of a substance in water. The relation between solubility curve and freezing point curve is shown in Fig. 25, for potassium chloride and water. The line AB gives the compositions and corresponding temperatures of solutions in equilibrium with ice. It is the freezing point curve. The line BC gives the compositions and corresponding temperatures of solutions in equilibrium with solid potassium chloride. It is the solubility curve. At the eutectic point B , we can have (at the fixed pressure of 1 atm.) the two solids and a liquid in equilibrium. The composition

of this liquid is definite (3.30 moles KCl per kilo of water). If heat is taken from this liquid, it freezes at constant temperature (-10.69°) to form an intimate mixture of crystals of ice and potassium chloride, called the eutectic mixture, or simply eutectic. Similarly the eutectic melts at constant temperature, like a pure solid. But, unlike a pure substance, the composition of the eutectic depends, even though very slightly, on the pressure.

The cooling curve and solubility-freezing point curve given in Figs. 24 and 25 are typical for simple systems. More involved curves are encountered when chemical combination takes place between solvent and solute, as for example, $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O} = \text{solid Glauber's salt}$, or $\text{HCl} + \text{H}_2\text{O} = \text{HCl}\cdot\text{H}_2\text{O} (\text{solid})$, or when two solid phases dissolve in one another to form a "solid solution," as do benzene and thiophene.

CHAPTER X

OSMOTIC PRESSURE

If a wet soluble salt is placed on a blister, the water is “drawn out” from the blister. The blister skin is not very permeable to most salts, but is rather rapidly permeated by water, and the water passes out from a dilute solution within the blister to the concentrated solution about the salt. That this might happen, and not the contrary movement of water, we should infer from the fact that the vapor pressure of water in the concentrated solution is less than that in the dilute solution, so that if blister fluid and saturated salt solution were to be placed in separate containers underneath a bell jar, the water would distill from higher to lower vapor pressure.

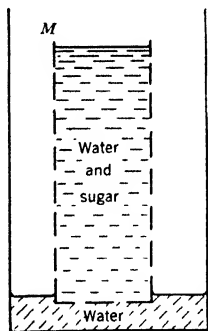


FIG. 26.—Osmosis.

47. Osmotic Pressure and Vapor Pressure.—When such a transfer of water can happen through the intervention of a vapor phase it may happen in some other manner, as by diffusion through a membrane. Nothing but experiment can tell us with what velocity

the transfer of water will occur. A knowledge of the relative vapor pressures will tell us whether a transfer is possible and, if so, in which direction.

Good semipermeable membranes permeable to water and not to sugar have been made by precipitating cupric ferrocyanide within the pores of clay tubes. In Fig. 26, *M* represents such a membrane. If a sugar solution is placed within the tube and the tube is dipped into pure water, water will diffuse into the tube and dilute the solution. The level of the sugar solution will rise, and the water will still enter in spite of the pressure

exerted by the column of sugar solution. If the sugar solution contains one mole of sucrose ($C_{12}H_{22}O_{11}$) per liter and the experiment is performed at 25° , it will require a pressure of 28 atm. upon the solution to prevent the entrance of water. A greater pressure will force water out from the solution; less will admit it. There is a pressure of 1 atm. on the water. The difference of pressure (27 atm.) which is just sufficient to maintain equilibrium is called the osmotic pressure.

Whenever one constituent of a solution passes through a membrane faster than some other, the flow of material is called osmosis.

Physical chemists usually call the osmotic pressure the osmotic pressure of the solution; biologists often call it more explicitly the osmotic pressure of the dissolved substance that cannot pass through the membrane. It is often necessary to be explicit.

When the solution under pressure is in equilibrium (with respect to transfer of water) with the pure solvent under a pressure of 1 atm., its vapor pressure at its temperature and pressure must be equal to that of the pure solvent at the same temperature and at a pressure of 1 atm. This follows from the principle laid down in Chap. VI, page 50, that two phases in equilibrium (with respect to a given type of transfer) with a third phase will be in equilibrium with each other (with respect to the same type of transfer). Hence, the effect of the increased pressure upon the solution is just enough to raise its vapor pressure up to the vapor pressure of the pure solvent.

In Chap. VI [page 52, Eq. (7)], an expression was found for the effect of pressure on vapor pressure. It was

$$RT \ln \frac{p_1'}{p_1} = v(p' - p), \quad (1)$$

where p_1 is the vapor pressure when the pressure on the solution is p , and p_1' is the vapor pressure when the pressure on the solution is p' . Let us take p to be the pressure on the pure solvent (usually 1 atm.). Then p_1 is the vapor pressure of the solution at 1 atm., and this must be increased to the value p_1' , the vapor pressure of the pure solvent, by increasing the pressure on the solution to the value p' . The difference, $p' - p$, is the difference of pressure on solution and solvent, required for equilibrium,

and is the value of the osmotic pressure, which we shall designate by π . Therefore an equation for the osmotic pressure is

$$\pi = \frac{RT}{v} \ln \frac{p_1'}{p_1}, \quad (2)$$

where p_1' and p_1 are the vapor pressures of the solvent and solution, respectively, when each is under the pressure of the solvent during the experiment (usually 1 atm.), and \ln means natural logarithm. For numerical calculations replace the symbol \ln with $1/0.4343 \log$. For the most precise calculations the partial molal volume of the solvent in the solution must be used for v , but for approximate calculations, or for dilute solutions, v may be taken to represent the volume of a mole of pure solvent.

48. A Simple Equation for Osmotic Pressure.—Equation (2) is more exact than we usually require. Suppose there is only one solute. Then the ratio of the vapor pressure of the pure solvent to that of the solution, when both are at the same pressure and temperature, is given by Raoult's law, and the more exactly, the more dilute the solution. Raoult's law is given as $p_1 = p_0 x_1$, where p_1 is the vapor pressure of the solution and p_0 that of the pure solvent [Eq. (2), page 61]. Using as above p_1' for the vapor pressure of the solvent we have from Raoult's law

$$p_1 = p_1' x_1$$

or

$$p_1'/p_1 = 1/x_1. \quad (3)$$

Hence,

$$\begin{aligned} \pi = \frac{RT}{v} \ln \left(\frac{1}{x_1} \right) &= \frac{RT}{v} (\ln 1 - \ln x_1) = -\frac{RT}{v} \ln x_1 = \\ &= -\frac{RT}{v} \ln (1 - x_2). \end{aligned} \quad (4)$$

Now the natural logarithm of $(1 - x)$

$$= -x + \frac{1}{2}x^2 - \frac{1}{3}x^3 \dots \quad (5)$$

For a dilute solution, x_2 is small compared with 1, so that a good approximation is given by taking the first term only of the series expansion:

$$\ln(1 - x_2) = -x_2 \text{ (approx.)}. \quad (6)$$

Substituting into Eq. (4) we obtain

$$\pi = \frac{RT}{v} x_2 = \frac{RT}{v} \cdot \frac{n_2}{(n_1 + n_2)}, \quad (7)$$

where n_1 and n_2 are the numbers of moles of solvent and solute, respectively, in the total volume V of the solution. When the solution is dilute, n_2 is small compared with n_1 and the equation

$$\pi = RTn_2/vn_1 \quad (8)$$

is a good approximation. Taking v for the dilute solution equal to the volume of a mole of solvent, vn_1 is the volume that would be occupied by the n_1 moles of solvent in the solution, and this is nearly equal to the total volume V in which n_2 moles of solute are dissolved. Making this final approximation we have finally a very simple equation for the osmotic pressure of substance 2 in a dilute solution:

$$\pi = RTn_2/V. \quad (9)$$

In the case of the solution of cane sugar in water, referred to above, n_2/V was one mole per liter. From Eq. (9),

$$\pi = 0.08206 \times 298.1 = 24.46 \text{ atm.},$$

whereas the observed osmotic pressure at 25° was 27 atm. A molal solution is not considered dilute, and for dilute solutions the agreement is better.

Notice that according to Eq. (9) the osmotic pressure is the same as the pressure that would be exerted by the n_2 moles of sugar if the sugar were an ideal gas (following the simple theory of gases) occupying the volume V . This remarkable fact was discovered experimentally. It made a great impression upon the chemists of the time. They promptly proceeded to explain as much as possible of physical chemistry by means of the idea of osmotic pressure, which they conceived as due directly to the impacts of the sugar molecules against the semipermeable wall. Their explanation of osmotic pressure in terms of the analogy to gases, though still occasionally taught to beginners in physical chemistry, is not entirely comprehensible, as the analogy is not perfect. Nowadays the concept of osmotic pressure is seldom used except when experiments on osmosis are under discussion.

For simplicity we assumed above that there was only one solute present. Suppose there is present in small quantity a third substance, which can pass through the membrane freely, like the water. Then Eq. (9) will still hold as an approximate relation for the osmotic pressure of the sugar. The third substance will at equilibrium come to nearly or quite the same concentration on both sides of the membrane, and will have practically the same effect on the vapor pressures of the sugar solution and of the solvent. Therefore the difference of pressure required to bring the vapor pressure of the solution with sugar up to the vapor pressure of the solution without sugar will be unaffected by the third substance, at least in dilute solutions. This difference we may call π_2 .

If the third substance cannot pass the membrane, but the water and sugar can, we shall similarly have an equation,

$$\pi_3 = RTn_3/V, \quad (10)$$

for the osmotic pressure of the third substance.

If both the sugar and the third substance cannot pass the membrane, but the water can, the mathematics which led to Eq. (9) can be modified accordingly, and will lead to the equation

$$\pi_{23} = \frac{RT(n_2 + n_3)}{V}, \quad (11)$$

for the total osmotic pressure due to substances 2 and 3. Hence,

$$\pi_{23} = \pi_2 + \pi_3. \quad (12)$$

In general, the total osmotic pressure, due to several substances which cannot pass the membrane, is equal to the sum of the several osmotic pressures due to each substance acting alone, provided that Raoult's law holds.

49. Plasmolysis.—If red blood cells are placed in pure water or in too dilute a solution they absorb water and swell until they burst. This is plasmolysis. In too strong a solution they lose water and volume. A solution in which they keep the same amount of water as they have in blood is called isotonic with the blood; stronger solutions are hypertonic; weaker solutions are hypotonic. Two solutions isotonic with the blood (or blood cell) are said to be isotonic with each other.

Such changes of volume are observed with many cells, even with plant cells protected by cellulose walls. In this case the cell expands against the wall or shrinks from it when placed in a solution not isotonic with it. Skins from the inner layers of small red onions (which can be bought at seed stores) furnish a convenient preparation for observation, which is best made with the aid of a microscope. Colored cells which do not change in volume when exposed to a variety of concentrations are dead, or at least have lost the semipermeability which seems to be necessary in the living cell. By observations of this kind it has been possible to find the comparative toxicity¹ of various chemical substances, such as the alcohols.

The cells are permeable to water, and impermeable or but slowly permeable to many other substances. When the cell is permeable to no component of a solution but the water, a simple theory can be given. Under these conditions the vapor pressure of water in the cell is equal to that of an isotonic solution. The vapor pressure of water in a hypertonic (stronger) solution is less than that in the cells, and the cell may therefore give up water to such a solution, and does so in fact.

The vapor pressure of a cell and of an isotonic solution is less than that of pure water at the same temperature. If for any reason we wish to make the vapor pressure of the cell equal to that of pure water we may put upon it a pressure equal to the osmotic pressure of the cell contents. Now it will require nearly the same pressure for the solution as for the cell contents [Eq. (2), page 80], as the partial molal volume of water will be nearly the same in the two cases. Hence the osmotic pressures of solutions isotonic with a cell permeable to water alone are approximately equal, when the osmotic pressures are measured in the ordinary way, by increasing the pressure on the solutions.

Increasing the pressure on the solutions changes their states, and changes their osmotic pressures. There is another way to make the vapor pressures of the solutions equal to that of water at the same temperature, namely, by decreasing the pressure on the water. By taking precautions against the formation of air bubbles, it is quite possible in fact to put a pull—that is, a negative pressure—upon liquids. The osmotic pressure of a

¹ With reference, of course, to the particular cell utilized.

solution is the difference of pressure upon it and upon pure water when they are in equilibrium with respect to transfer of water at a given temperature. When a cell and a series of solutions have the same vapor pressure of water, all being under the atmospheric pressure, it will require the same negative pressure upon pure water to make it in equilibrium with any of them, that is to say, they all have the same osmotic pressure when they are in their natural state at 1 atm.

As regards Eq. (2) and the approximate Eq. (9), these give in fact the osmotic pressure of the solution when it is under the normal atmospheric pressure, when, as is ordinarily the case, the volume of a mole of solvent is used for v instead of the partial molal volume. It is possible to correct the measured osmotic pressure (the solution is then under the osmotic pressure plus 1 atm.) to obtain the osmotic pressure of the solution when under atmospheric pressure.¹ The correction is usually small.

When solutions are isotonic with a cell permeable to water alone, their osmotic pressures when under normal atmospheric pressure are exactly equal, like their vapor pressures of water.

If the semipermeability of the cell is not perfect, the composition of the cell contents may not be the same when it is in equilibrium at the same volume with two different solutions in succession. Hence its vapor pressure need not be the same, and therefore the vapor pressures, and also the osmotic pressures, of isotonic solutions need not in this case be equal.

Under the influence of physical chemists of an earlier generation, many biologists still like to discuss such topics as plasmolysis in terms of osmotic pressure. It is evident from the preceding that plasmolysis and isotonicity are more directly and simply explained in terms of vapor pressure. It has been calculated that the blood of mammals has an osmotic pressure of about 8 atm. Students may imagine from this that the blood is under some such great pressure, or that possibly a pressure of 8 atm. is lurking within the blood, seeking to manifest itself. Both ideas should be rejected together. All that is meant by the 8 atm. is that this is the pressure that would be required upon blood to bring its vapor pressure up to the value for pure water at body tempera-

¹ MACDOUGALL, F. H., "Thermodynamics and Chemistry," 2d ed., p. 215, Eq. (43), John Wiley & Sons, Inc., New York, 1926.

ture. In the animal body there is no pressure of 8 atm.,¹ nor is there any pure water.

50. The Osmotic Pressure of the Colloids of Blood Serum.—

The colloids of blood serum are those constituents that cannot diffuse through a membrane, such as wet parchment, which permits freely the diffusion of water and of "crystalloids" such as salts, sugars, acids, etc. The osmotic pressure of the colloids is that excess pressure required upon a solution containing them to bring the solution into equilibrium (with respect to transfer of water and of diffusible constituents) with a solution containing the diffusible constituents but without the colloids. The meaning of this will be made clearer by considering an experiment to measure the osmotic pressure of the colloids. Figure 27 represents a tube *M* made of semipermeable material. We place the blood serum (blood deprived of red cells by coagulation) in the tube, and dip the tube into a solution whose composition is as nearly the same as that of serum, but without the colloids, as we know how to make it. Diffusion takes place, and the composition of the external solution approaches that of the colloid-free serum, while the serum becomes weaker,

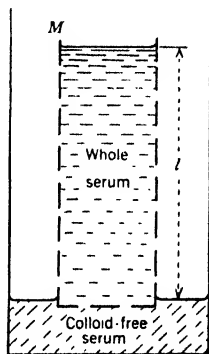


FIG. 27.—Osmotic pressure of blood colloids.

due to the influx of water, and changes in other respects. After the level of the serum ceases to change, we replace the contents of the tube with a fresh sample of serum, filling up the tube to the new level. This time the composition of the serum will not change so much when diffusion takes place, and by repetition we can ultimately find the difference of level *l*, when the serum in the tube has the same composition as a fresh, unchanged sample. The pressure difference corresponding to this difference of level can easily be computed in terms of a column of ice-cold

¹ The (systolic) blood pressure required to force blood into an artery in the human arm is about 120 mm. of mercury (from 90 to 150 in normal young adults). The (diastolic) pressure of the blood leaving the corresponding vein is about 65 mm. These pressures are the excess over the atmospheric pressure.

mercury from the density of the mercury (13.596) and that of the serum, which need not be known very exactly, as the pressures are small and incapable of very exact biological interpretation.¹

This pressure difference is the osmotic pressure of the colloids of the serum. Since the lowering of the vapor pressure of water (at 1 atm.) in the whole serum is greater than that in the colloid-free serum, the extra pressure has to be put on the whole serum, as shown in Fig. 27.

The osmotic pressure of the colloids of blood serum has been found to be about 30 to 34 mm. of mercury. In earlier work somewhat lower values were found (25 to 30 mm.). Although the osmotic pressure of the blood has no great significance, it is otherwise with the osmotic pressure of the blood colloids. It is an important task of the kidneys to remove water and many crystalloids from the blood while retaining the albuminous blood colloids. In the glomerulus of the kidney a filtration occurs, in which colloids are retained and water and crystalloids are permitted to pass. The existence of a more or less perfect semi-permeable membrane in the glomerulus is evident. Unless the pressure on the blood entering the glomerulus is greater than the osmotic pressure of the blood colloids there will be no tendency for the water to leave the colloids and enter the filtrate. The pressure of the blood is normally ample to account for the filtration. In experiments on animals it has been possible to reduce the blood pressure in the renal artery to a value near the osmotic pressure, and when this is done, the secretion of urine stops.

The variation in blood pressure from artery to vein is also quite enough to be important in determining the interchange of fluid between blood and lymph.

It is fortunate that the osmotic pressure of the blood colloids can be directly measured, as the calculation presents some difficulties. These are in part due to the fact that the concentration of the crystalloids need not be the same on both sides of the membrane in Fig. 27 at equilibrium, even if all solutions are dilute. When the colloid or other non-diffusible constituent

¹ It is of course possible to apply the excess pressure by means of a column of mercury of known density, instead of using a difference of level of a column of serum.

consists of positive or negative electrically charged particles, which is often the case with colloids, the concentration of electrolytes such as sodium chloride will not be even approximately equal on both sides of the membrane when equilibrium is reached, even if the solutions are extremely dilute. Hence the lowering of vapor pressure by the electrolytes is not the same on both sides of the membrane, and the excess or osmotic pressure required for equality of vapor pressure depends on the effect of the electrolytes in lowering vapor pressure as well as on the effect of the colloids.

The concentration effects, produced by non-diffusible components bearing an electrical charge, will be discussed under the heading Donnan equilibrium (Chap. XXV).

51. The Rise of Sap in Trees.—Trees take in great quantities of water through their roots, from a very dilute water extract of the soil, and evaporate the water through their leaves. The sap rises to great heights against the force of gravity. An interesting question is, does the tree have to do work to accomplish the transfer of water from soil to the air at the height of the leaves? This all depends on the relation between the vapor pressure of water from the soil and the partial pressure of water in the air. Let the partial pressure of water in air at the height of the leaves be p_1 . Then the partial pressure of water in an air mixture at ground level, when the lower air mixture is in equilibrium with the upper with respect to transfer of water, would be higher than p_1 by the small weight of a column of pure water vapor of unit cross-sectional area, which water vapor is at the pressure p_1 at the top of the column. Let the weight of this column be w . Then if the vapor pressure of water from the soil exceeds $p_1 + w$, water would of itself tend to evaporate and rise to the height of the leaves, and the tree would have to do no work to accomplish this overall result, though work might have to be done in the application of imperfect mechanisms. Under normal conditions the tree may even be able to utilize a positive tendency towards evaporation to do other kinds of work.

The semipermeable membrane furnishes a device by means of which the tree may effect transpiration of water, and a large part at least of the rise of sap in trees can be explained by the osmotic pressure of the sap. Thus the natural sap of the sugar

maple is stated to contain from 2 to 3 per cent of sucrose, together with smaller quantities of proteins, malic acid, and inorganic constituents. Calculation shows that a 3 per cent solution of sucrose has at 0°C. an osmotic pressure of 1.989 atm., which corresponds to a height of the sap (density of 3 per cent cane sugar solution is 1.0121) of 66.6 ft. Thus the sap could rise to this height on account of the osmotic pressure of the sucrose alone, if a semipermeable membrane containing it were placed in pure water. The soil extract is not pure water but is very dilute, and the solutes of the soil, in so far as they pass through the roots, do not hinder the passage of water. The osmotic pressure is evidently one of the important factors in transpiration.

Problems

1. Verify (*a*) the calculation of the osmotic pressure of the sap and (*b*) of the height in feet; use Eq. (9). The density of ice-cold mercury is 13.596. There are 3.28 . . . ft. per meter. A precision of 1 per cent in the calculation is sufficient.
2. Assuming that the roots are impermeable to sea salt, suggest a reason why the growth of trees close to salt water is often stunted.

CHAPTER XI

THE COLLIGATIVE PROPERTIES OF SOLUTIONS OF ELECTROLYTES AND OF NON-ELECTROLYTES

In this chapter some of the evidence will be reviewed which led physical chemists to the idea that electrolytes in water solution are more or less completely ionized.

52. The Colligative Properties.—The lowering of vapor pressure by introduction of a dissolved substance, the elevation of boiling point, the depression of freezing point, and the osmotic pressure due to the solute are all intimately connected, and are for that reason called the colligative properties. From Eqs. (3), (4), and (5) of Chap. IX, and Eq. (7) of Chap. X, x_2 can be eliminated, giving the equations

$$\frac{p_{01} - p_1}{p_{01}} = \frac{\Delta_{bp} L_{vap}}{RT^2} = \frac{\Delta_{fp} L_{fus}}{RT^2} = \frac{\pi v}{RT} \quad (1)$$

These equations can be used to calculate any one of the colligative properties from any other, provided the solution is dilute, and we have the necessary latent heats and the volume of a mole of solvent. From thermodynamics more exact, but also more complicated, relationships can be derived; these require a knowledge of other properties of the solution.

From the mole fraction any one of these properties can be calculated. It is unnecessary to know anything about the solute but its molecular weight, as from this and the molecular weight of the solvent the mole fraction can easily be calculated from the weight percentage.¹

Now this is a very important fact. It means that the thing that counts in these colligative phenomena is not the kind of

¹ The molecular weight of the solute is the one usually found for it in handbooks, and in the case of organic chemical substances the assigned molecular weight was determined in fact with the aid of some one of the formulas given in Chaps. IX and X.

molecule added to a solvent but only the number of molecules added. When several kinds are added, the total number of molecules determines the lowering of vapor pressure or other effect.

53. The Colligative Properties and Ionization.—When therefore it was regularly observed that the effect of a mole of dissolved salt, strong acid, or strong base is several times as great as the effect of a mole of sugar or other such organic substance, the suggestion was in order that the molecular weights of these substances are abnormal, and that the molecular weight given by the chemical formula is somehow wrong. Arrhenius was particularly struck with the fact that solutions of many of these substances conduct electricity. He measured for a large number of substances the ratio of the observed freezing point depression Δ_{obs} divided by the theoretically calculated depression Δ_{cal} for a solute in a solution obeying Raoult's law. For such solutes the depression Δ_{cal} is 1.89 times the concentration in moles per liter. The ratio $\Delta_{\text{obs}}/\Delta_{\text{cal}}$ is called the van't Hoff coefficient i . Table I shows the values of Δ_{obs} and i for various concentrations of sodium chloride in water solution, according to early measurements.

TABLE I.—VAN'T HOFF COEFFICIENT FOR NaCl

Formula weights per liter	Δ_{obs}	i
0.0467	0.117	2.00
0.117	0.424	1.93
0.194	0.687	1.87
0.324	1.135	1.86
0.539	1.894	1.85

As indicated by Table I, the coefficient i , for sodium chloride in water, increases with dilution of the solute, becoming equal to about 2 as the concentration approaches zero. Similar results were obtained for other electrolytes. Thus i for Na_2SO_4 in water seems to approach the value 3, and that for MgSO_4 , the value 2 at zero concentration. Arrhenius explained at one stroke the main facts relating to Raoult's law deviations and electrical conductivity. He suggested that the solutes that make a water

solution conducting are dissociated in water solution into charged ions. These ions conduct the electric current. They are as effective in lowering vapor pressure and in producing the other colligative effects as an equal number of ordinary molecules. The degree of ionization depends on the dilution, becoming 100 per cent at infinite dilution (at zero concentration). Thus sodium chloride should produce in extremely dilute solutions twice the effect of a non-electrolyte. This is borne out by Table I. Sodium sulphate is dissociated into two sodium ions and one sulphate ion; the sulphate ion carrying twice as much electricity as a sodium ion (since the solution as a whole is not charged electrically). By assuming that the effectiveness of the ions in carrying current does not depend on the concentration he was able to calculate the degree of ionization from the electrical conductivity, and from this the van't Hoff coefficient. The coefficient so calculated was found in general to be in agreement with that determined from the freezing point measurements.

The work of many investigators led to the general acceptance of the views of Arrhenius. The sodium ion is supposed to be an atom of sodium which has lost an electron and thus acquired a positive charge. Due to this charge it has entirely different chemical properties from those of metallic sodium. In some respects the theory of Arrhenius is now known to be too simple; in particular, the effectiveness of an ion in carrying current is now believed to be greatly dependent on the concentration and on the presence of other ions. It is no longer believed that Raoult's law is as good when applied to ions as when applied to non-electrolytes. These modifications apply with the greater force to the ions of strong (that is, largely dissociated) electrolytes, and the original views of Arrhenius are still applied to weak electrolytes (acetic acid, ammonium hydroxide, etc.) with a considerable degree of success.

CHAPTER XII

ELECTRICAL CONDUCTANCE

54. Definitions.—When the electrical conductance of solids or of pure liquids is measured, the result is expressed in terms of the resistance of a cube, each of whose edges is 1 cm. long. The resistance of such a centimeter-cube is called the specific resistance, and the reciprocal of this number is called the specific conductance.¹ When the shape is not that of a cube and the dimensions not 1 cm., the resistance is directly proportional to the distance over which the current must pass, and inversely proportional to the cross-sectional area through which it must pass.

For solutions, it is necessary to take account of their concentration. Pure water has a very high specific resistance, which is 26×10^6 ohms at 18° , corresponding to a very low specific conductance of 0.038×10^{-6} mhos. (A mho is one reciprocal ohm). Solutions of electrolytes as ordinarily encountered have conductances much greater than that of pure water, and, at least in dilute solutions, the specific conductance is the greater, the more electrolyte the solution contains.² It is the usual practice to take account of the concentration by dividing the specific con-

¹ Some authors call the specific resistance the resistivity, and the specific conductance the conductivity. But the word conductivity is often used to denote the ability of some body to conduct the electrical current without reference to the shape or dimensions of the body, just as we have used the word conductance. The word specific does not imply a reference to any standard substance, such as water. Once, it always implied such reference to a standard substance, usually water; now it rarely does.

² In very strong solutions the effect is often reversed, so that the specific conductance passes through a maximum. This maximum often occurs at about five equivalents per liter; in the case of sulphuric acid it occurs at about eight equivalents per liter. Pure sulphuric acid is practically a non-conductor, as is pure water itself, so that a maximum must occur, as the liquids are miscible in all proportions. A maximum is generally seen in aqueous solutions of any electrolyte, provided it is sufficiently soluble.

ductance L due to the electrolyte (subtracting when necessary the small conductance of the water used) by the number of gram equivalents of electrolyte present in the cubic centimeter. The quotient is called the equivalent conductance Λ (Greek capital lambda). The concentration is, however, customarily expressed by chemists as normality c , in gram equivalents per liter. Hence there are $c/1,000$ gram equivalents in the cubic centimeter and we have the obvious relation

$$\Lambda = L \div (c/1,000) = 1,000L/c. \quad (1)$$

Sometimes it helps to think of the equivalent conductance as being the actual conductance that would be observed if a whole gram equivalent of electrolyte were placed (with the accompanying water) between two parallel conducting plates 1 cm. apart and of sufficient area to hold the volume of the solution containing the gram equivalent. The correctness of this is easily seen. Since c gram equivalents occupy one liter, or 1,000 cc., the one gram equivalent in the cell will occupy $1,000/c$ cc., and will therefore spread out over an area of $1,000/c$ sq. cm. Now the conductance is directly proportional to the area, and the actual conductance of the large cell will be $1,000/c$ times L , L being the conductance of a centimeter-cube. Hence, from Eq. (1), the actual conductance of such a large cell is equal to Λ , the equivalent conductance.

55. The Measurement of Conductance.—The equivalent conductance is calculated from the normality and the measured specific conductance. This can be measured in a cell whose dimensions are not known; it needs merely to be of good design. The specific conductance of solutions of potassium chloride has been carefully studied at various concentrations and temperatures,¹ and the specific conductance of some other solution can be determined by measuring the actual conductance of it and of a standard potassium chloride solution when placed successively in the same cell. The solution which shows in this cell x times the actual conductance of the potassium chloride solution has a specific conductance x times that of the potassium chloride solution.²

¹ See "International Critical Tables," Vol. 6, p. 230.

² Provided that the cell is properly designed. It is well to compare the solution to be studied with a potassium chloride solution of about the same conductance.

The actual conductance of the cell is equal to the reciprocal of the actual resistance, which is usually measured by means of a Wheatstone bridge circuit. The network is shown in Fig. 28. To avoid electrolysis, alternating current is used—formerly furnished by a small induction coil and lately furnished by a heavy-duty vacuum tube oscillator. An induction coil does not furnish pure alternating current, nor a single frequency of oscillation. R_1 and R_2 are fixed resistances, often chosen equal. R_x is the cell of unknown resistance and R is the variable known resistance.¹

When R is properly adjusted, no current passes through the telephones t . The condition for this is, that there is no difference

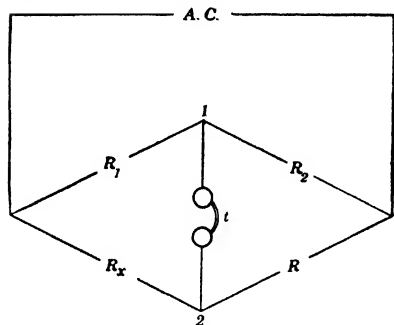


FIG. 28.—Wheatstone bridge circuit.

of potential between points 1 and 2. If direct current were supplied, the condition for no difference of potential and therefore for no current or sound in the telephones would be simply

$$R_x/R_1 = R/R_2. \quad (2)$$

Since alternating current is actually supplied, the electrical capacity and inductance in the four arms of the bridge are also of importance. For zero current in the telephones the resistances must be balanced, satisfying Eq. (2), and the reactances due to inductance and capacity must also be balanced. The reactances can generally be balanced by inserting capacities in parallel with some of the resistances. The success of this operation is judged by the sharpness with which that value of R can be determined which gives the least sound in the telephones. It can happen that the body of the experimenter carries enough current, due to its capacity, to affect the measurements. In precise measurements some method of grounding important points in the circuit is necessary, and a system of screening

¹ There is no particular virtue in the exact sequence of resistances shown in the figure, and the wires leading to the source of current at A. C. and to the telephones may be interchanged.

the apparatus against the action of external electrical effects is advisable.¹

The cell for the measurement of resistance consists usually of two platinum plate electrodes firmly held in place by stiff platinum wires in a vessel of suitable shape. The area of the electrodes and their distance apart vary according to the conductance of the electrolyte solution that the cell is designed to measure. The electrodes are usually coated with platinum black by electrolysis of a solution of "platinic chloride," with or without a trace (say, 0.1 per cent) of lead acetate.²

56. The Conductance of Solutions of Various Electrolytes.—The substances that impart to water any considerable degree of conductance are acids, bases, and salts. Nearly all salts produce solutions of relatively high conductance, which varies with the concentration and with the kind of salt. The halides of cadmium and of mercury are exceptional, and produce solutions of low conductance. These salts are called weak.

The strong acids and bases furnish relatively highly conducting solutions. Some of them are sulphuric, nitric, and the halogen acids (except HF), potassium and the other alkali hydroxides, calcium hydroxide and the hydroxides of the other alkaline earths, and organic bases such as tetramethyl ammonium hydroxide.

Some important acids and bases of intermediate strength are phosphoric, formic, and trichloroacetic acids, and some organic substitution products of ammonium hydroxide and other bases.

Some weak acids and bases are sulphurous, nitrous, hydrofluoric, and boric acids, and hydrazine (N_2H_4) among inorganic compounds. All the monobasic carboxylic acids of organic chemistry (containing the $-\text{COOH}$ group) are weak, except those, like trichloroacetic acid, that contain acid-forming elements (such as chlorine). Phenols, such as carbolic acid ($\text{C}_6\text{H}_5\text{OH}$), are usually weak acids. Carbonic acid and ammonium hydroxide are usually reckoned as weak; in these cases the concentration of the solution is computed by assuming that all of the dissolved CO_2 or NH_3 has reacted with the water to form H_2CO_3 or NH_4OH .

¹ For methods of grounding, of electrical screening, and a description of the electrical apparatus and its theory, see Shedlovsky, *J. Am. Chem. Soc.*, **52**, 1793 (1930), and Jones and Josephs, *J. Am. Chem. Soc.*, **50**, 1049 (1928).

² For a recent study of cells, see Jones and Bollinger, *J. Am. Chem. Soc.*, **53**, 411 (1931), and Shedlovsky, *J. Am. Chem. Soc.*, **52**, 1806 (1930).

The strength of a polybasic acid depends on the stage of ionization under discussion. Thus, when dissolved in water, H_3PO_4 is fairly strongly ionized to $\text{H}^+ + \text{H}_2\text{PO}_4^-$, but only weakly further ionized to the stage at which HPO_4^{--} is formed.

The classification into strong, weak, and intermediate electrolytes is not a perfect one. Considerable difficulty would be found in many cases in deciding whether a particular acid should be called weak or intermediate. The intermediate class includes those substances that are not clearly strong nor weak. The importance of such a classification arises from the fact that some simple rules can be given for solving certain problems of equilibrium if the electrolyte is strong, and other rules can be given if the electrolyte is weak. If the electrolyte is neither definitely strong nor weak, no simple rules can be given at present.

57. Equivalent Conductance and Dilution. The Degree of Ionization.—If we measure the equivalent conductance of any electrolyte at various dilutions, starting with a solution not too strong,¹ we find as the dilution of the solution is increased by the addition of water that the specific conductance L does not decrease so fast as the concentration c (in equivalents per liter). That is to say, the ratio L/c increases with dilution, and therefore the equivalent conductance Λ ($= 1,000L/c$) likewise. When Λ is plotted against c (or against the square root, cube root, or logarithm of c) an important difference between weak and strong electrolyte becomes evident. Of course, at *any* given concentration the equivalent conductance (and also the specific conductance) of the strong electrolyte is greater than that of the weak electrolyte. In very dilute solutions, however, the weak electrolyte shows a tendency to gain on the strong. Figure 29 (page 97) shows the equivalent conductances of hydrochloric and acetic (HAc) acids at various concentrations. In order to compare the two acids over a considerable range of concentration, Λ is plotted against the cube root of the concentration. The scale of the cube root is numbered from right to left, so that the dilution increases from left to right. Observe that the curve for HCl indicates that the equivalent conductance does not rise indefinitely, but is proceeding towards a value of about 380

¹ That is, if there is a solution of maximum conductance, we shall start with a solution less strong than it.

at zero concentration. A value of Λ for zero concentration will be denoted by Λ_0 . In the case of the curve for HAc it would on the other hand never be possible to judge from the measured points (along the full line) where the curve might intercept the axis of zero concentration. Experimental difficulties make it impossible to continue measurement of Λ much further than the last point shown (for which $c = 0.0001$). It should be especially noted that the value of Λ_0 for acetic acid has not been determined from conductance measurements of acetic acid solutions; it has been calculated by means of an indirect method to be given below.

The two curves given in Fig. 29 are typical for strong and weak electrolytes. Some electrolytes give intermediate results. The *limiting equivalent conductance* Λ_0 can be determined directly from the curves of conductance measurements in the case of strong electrolytes, but not in the case of weak electrolytes.¹

The electrical conductance is believed to be due to the motion of the ions in the electrical field between the plates of the conductance cell. Each ion, as it moves, carries a positive or a negative charge. Even the very small conductance of pure water is believed due to the presence of very small concentrations of hydrogen ions and hydroxyl ions. There is no doubt that the greater conductance of hydrochloric acid solutions is due to the fact that hydrochloric acid is more extensively ionized than

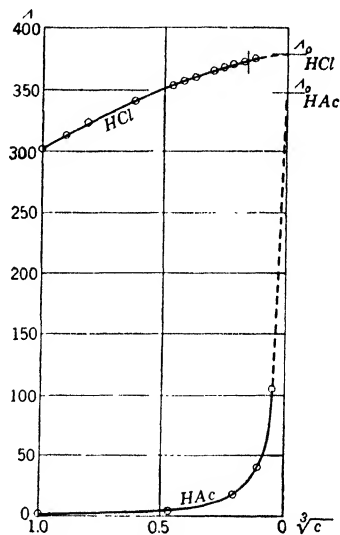


FIG. 29.—The equivalent conductance at 18°C. of hydrochloric—typically strong—acid, and of acetic—a typically weak—acid, plotted against the cube root of the concentration in equivalents per liter.

¹ It should go without saying that there is always something arbitrary about an extrapolation, or continuation of a curve beyond the measured values. The very precise location of the limiting values is a matter for the specialist, who uses all possible data and principles to reduce arbitrariness.

acetic acid. When we consider the change of the equivalent conductance with dilution we must remember, however, that there are two possible causes for this change. The degree of ionization may increase with dilution, or the velocity of the moving ions under the same applied voltage may increase. Both causes are believed to be operating, but when the electrolyte is definitely strong or weak, one cause appears to predominate over the other.

When the electrolyte is weak, the predominating cause for the increase of Λ with dilution is simply an increase in the percentage ionization. As the concentration approaches zero, the degree of ionization approaches 100 per cent. Suppose that the equivalent conductance at a certain dilution is only one-tenth of the value at infinite dilution. Then the degree of ionization at the given dilution is evidently one-tenth of 100 per cent, that is, 10 per cent. The ratio, Λ/Λ_0 , of the equivalent conductance at a given dilution to that at zero concentration, is called the conductance ratio. This is equal to the fraction ionized, α , under the assumption, justified for weak electrolytes, that the effectiveness of a gram equivalent of a given electrolyte in carrying electricity through the solution depends only on the number of ions, the velocity of these ions being independent of the dilution. This gives the equation

$$\alpha = \Lambda/\Lambda_0. \quad (3)$$

It will be shown later how the conductance ratio can be used to determine the mass action constant for a weak electrolyte. In the meantime, it should be obvious that the hydrogen-ion concentration of a solution of acetic acid in water can be calculated from the conductance ratio for the solution and its normality (in equivalents per liter).

For a period of years it was believed that the change of Λ with dilution in the case of strong electrolytes, such as HCl, might be explained in the same way, or with but slight modifications. This has been proved not to be the case. On the contrary, the increase of equivalent conductance of solutions of strong electrolytes with dilution is now held to be principally or wholly due to an increase in the velocity of the moving ions. The degree of ionization is held to be nearly or quite 100 per cent. Thus

solutions of HCl have, at equal normality, many more ions per liter than solutions of acetic acid. The ions are therefore closer together, and in strong solutions of HCl the ions are closer together than in weak solutions. When the ions are on the average very close to one another, any given moving ion is under the influence of the electrical field due to the ions themselves as well as the field due to the voltage on the plates of the conductance cell. Hence the velocity of a given ion under a definite voltage may be affected by the near presence of other ions and may therefore be expected to vary with the dilution. The development of this idea by means of electrical theory has been carried out by Debye and Hückel. Their theory calls for a decrease in velocity, and hence of equivalent conductance, with increasing strength of the solution, and is in agreement with observation, at least when the solutions are not too strong.¹

58. A Method for Calculating Λ_0 for a Weak Electrolyte.—Let us take for example acetic acid, HAc. At zero concentration it is supposed completely ionized into $H^+ + Ac^-$, and the ions are supposed at zero concentration to have no influence on one another, even in the case of strong electrolytes. Hence the limiting equivalent conductance of the electrolyte may be supposed due to the joint action of the ions which go to make up the electrolyte, and each of these ions may be supposed to have its own equivalent conductance at zero concentration. In the following, the subscript zero will be omitted for simplicity, but all the conductances refer to zero concentration, as it is only at zero concentration that it is permissible to discuss (in a simple manner) the equivalent conductances of individual ions. The limiting equivalent conductance of acetic acid, now written Λ_{HAc} , is equal to the sum of the limiting equivalent conductances

¹ In Fig. 29 a short vertical line has been drawn through the HCl curve between the last two points on the right. This indicates the solution of hydrochloric acid that has, according to our theory, the same number of ions per liter as the strongest acetic acid solution shown (one normal). In this hydrochloric acid solution the ions are the same average distance apart as in the normal acetic acid solution. Since in this hydrochloric acid solution the ions are already so far apart that further dilution changes the equivalent conductance but very little, and in all the acetic acid solutions shown the ions are at least this far apart, it is evident that the theory is consistent in explaining the variation of equivalent conductance in the case of acetic acid as due principally to the change of the degree of ionization.

of its ions, $\Lambda_{H^+} + \Lambda_{Ac^-}$. Similarly for other electrolytes. Now the acid HCl and the salts NaCl and sodium acetate (NaAc) are all strong, so that the equivalent conductances at zero concentration of these substances can be determined by extrapolation of curves such as for HCl in Fig. 29. We have the equations

$$\Lambda_{HAc} = \Lambda_{H^+} + \Lambda_{Ac^-}, \quad (4)$$

$$\Lambda_{HCl} = \Lambda_{H^+} + \Lambda_{Cl^-}, \quad (5)$$

$$\Lambda_{NaAc} = \Lambda_{Na^+} + \Lambda_{Ac^-}, \quad (6)$$

$$\Lambda_{NaCl} = \Lambda_{Na^+} + \Lambda_{Cl^-}. \quad (7)$$

By addition of Eqs. (5) and (6) and subtraction of Eq. (7) together with consideration of Eq. (4) we have

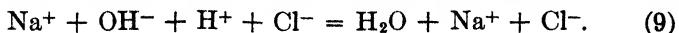
$$\Lambda_{HAc} = \Lambda_{HCl} + \Lambda_{NaAc} - \Lambda_{NaCl}. \quad (8)$$

In this way the limiting equivalent conductance of a weak electrolyte can be calculated from the limiting equivalent conductances of strong electrolytes. The method can be applied to weak bases or weak salts.

From conductance measurements alone only the sums of the equivalent conductances of the ions, such as $\Lambda_{H^+} + \Lambda_{Ac^-}$, can be determined. But by combining conductance data with transference numbers (Chap. XIV) the limiting equivalent conductances of the separate ions can be calculated. These are given in tables, and from such tables the limiting equivalent conductance of a weak electrolyte can naturally be calculated, and somewhat more conveniently than by the use of the method given above.

59. Some Consequences of Ionization.—It is unnecessary here to refer to all the facts which suggested originally the hypothesis of ionization, but it will be well to recall some important facts which are explained by it.

When a strong acid is neutralized by a strong base, both in dilute solution, the heat given out is about 14,000 gram-calories per mole of water formed, and is about the same, no matter what strong acid is neutralized, and by what strong base. The reason for this is clear. Both acid and base are nearly or quite wholly ionized, so that the equation for the reaction may be written

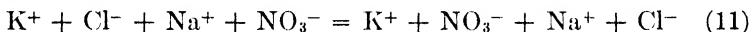


The water is ionized practically not at all, but the salt is ordinarily strong. But this equation amounts to the following:



The equation for any other strong acid and strong base will reduce to Eq. (10) and therefore the figure 14,000 refers simply to the combination of hydrogen ions with hydroxyl ions to form a mole of water.

When two (strong) salts are mixed in dilute solution, an equation such as



reduces to no reaction at all. The heat of mixing is in fact nearly zero; this is what is meant by the thermoneutrality of salts.

Salts, acids, and bases behave in the usual operations of qualitative analysis¹ as if each contained independent constituents. Thus any (true) chloride gives a precipitate with silver nitrate, independently of the metal with which it was combined. But many organic substances give no test with silver nitrate unless first decomposed. Such substances are not electrolytes. The silver nitrate test is a test for chloride ion, and not for the chlorine atom.

The effects of electrolytes on living substance are often interpretable as effects of their ions. For instance, the effect of acids is mainly due to the hydrogen ion; the disinfectant action of mercury salts appears to be due mainly to the mercuric ion. The parallelism between physiological action and ionization is not always perfect, and in many cases the action of an undissociated molecule may be as important as that of the ions. It is believed that sometimes an uncharged molecule can enter the biological cell more readily than the ions.

Problems

1. (a) From Fig. 29 and the text, estimate the percentage ionization of acetic acid in 0.0001 normal solution. (b) What would be the corresponding normality of the solution in hydrogen ions? (c) What would be the normality of a solution of HCl which has the same hydrogen-ion concentration as the 0.0001 normal acetic acid solution?

¹ By the "wet way," *i. e.*, in water solution.

2. Which ion travels faster in extremely dilute solution under the action of the same electrical voltage, chloride ion or acetate ion? All ions of equal valence carry the same charge of electricity.

3. (a) The limiting equivalent conductances for HCl, NaCl, HNO₃, and NaNO₃ are in round numbers 380, 108, 377, and 105, respectively, at 18°. By how much does the equivalent conductance of H⁺ exceed that of Na⁺ at zero concentration? (b) The limiting equivalent conductance for NaAc is 78. Calculate it for acetic acid.

4. The limiting equivalent conductance for NaOH at 18° is 217. Using a similar principle, calculate the limiting equivalent conductance for HOH. This is the conductance that would be measured if one liter of water containing one equivalent each of H⁺ and OH⁻ were placed between parallel electrodes one centimeter apart. Division by 1,000 gives the specific conductance L of such a hypothetical solution. Water does not of course contain ions in any such concentration, and the measured value of L is 3.8×10^{-8} for pure water at 18°. Calculate the normality of the hydrogen ions in pure water to two significant figures.

CHAPTER XIII

THEORY OF THE CONDUCTION OF ELECTRICITY THROUGH AQUEOUS SOLUTIONS

The conduction of electricity through metals is believed to be due to the motion of free electrons in the metal. The electron is the unit, or atom, of negative electricity.¹ The conduction of electricity through solutions takes place ordinarily in a very different way; only in such an unusual case as that of metallic sodium dissolved in liquid ammonia (anhydrous) is there any evidence of the presence of free electrons. In all water solutions the electricity is carried along with material substance in the form of ions, and at the electrodes the ions lose their charges by rejecting or accepting electrons.

60. The Migration and the Discharge of Ions.—The electricity may be passed along by the motion of a chloride ion, Cl^- , or, equally well, by the motion of a sodium ion, Na^+ . Since the former is a chlorine atom with an excess electron, and the latter is a sodium atom with a deficit of one electron, a motion of Na^+ in a given direction is equivalent to an equal motion of Cl^- in the opposite direction, so far as the conduction of electricity is concerned. In the preceding chapter we learned that different ions such as Cl^- , Ac^- , NO_3^- , etc., do not have the same velocity at zero concentration, nor do different positive ions. There is no reason why the Na^+ ion in a dilute solution of NaCl should move just as fast as the Cl^- ion and therefore carry an equal share of the current; and in fact the two ions of an electrolyte usually carry substantially different shares of the current.

When a little electricity is passed through the solution, an individual sodium ion does not travel all the way through the solution from one electrode to the other. The motion is rather

¹ Its magnitude is 1.592×10^{-19} coulombs. When a current of one ampere is flowing through a wire the quantity of electricity which passes a given section of the wire per second is 1 coulomb.

slow, but every sodium ion slips along a little in one direction in a sort of irregular procession or migration, while every chloride ion is slipping a bit in the opposite direction. These displacements effect a transfer of electrons which constitutes a flow of electrical current.

What we shall call the positive current, or simply current, flows in the solution in the direction in which the current is viewed by electricians as flowing.

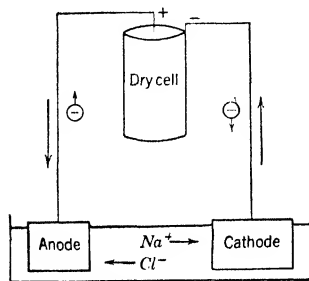


FIG. 30.—The directions of current, electrons, and ions in electrolysis.

The positive ions like Na^+ migrate in this direction, and the negative ions migrate in the opposite direction. In the ordinary dry cell the center electrode of carbon is always termed the positive terminal, and the zinc is the negative terminal. Figure 30 illustrates the conventions, and must be thoroughly learned. The long arrows along the wires show the direction of the (positive) current. The minus

sign within a small circle represents an electron, and the small arrow attached to it shows the direction of the flow of electrons. The direction of flow of the ions is also shown. Within the cell containing the sodium chloride solution (as within any cell whatever) the (positive) current flows from *anode* to *cathode*; this defines these terms. The positive ions move towards the cathode,

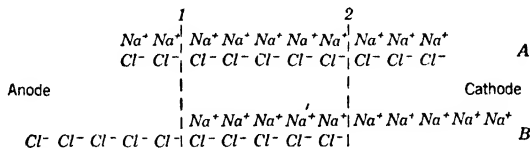


FIG. 31.—The unequal movement of ions in electrolysis.

and are called *cations*; the ions with negative charges move towards the anode, and are called *anions*.

During the flow of current any portion of the solution (large enough to contain a considerable number of ions) remains electrically neutral. Figure 31 shows how this can be, in spite of the fact that the two ions do not travel with equal velocity.

Consider a portion of the solution between the two imaginary cross sections 1 and 2. Figure 31A shows an arrangement of ions before the current is passed, and Fig. 31B, a possible arrangement after some current is passed. Observe that the number of cations which have left the portion is not equal to the number of anions which have left, but as many cations have entered as left, and the same is true of the anions. This leaves the portion neutral.

The anode portion and the cathode portion also remain neutral, but the figure does not show how. If nothing else happened, there would in fact be an excess of five cations in the immediate neighborhood of the cathode, and an equal excess of anions about the anode. The excess is in both cases taken care of by a flow of electrons to or from the wire. Five electrons enter the solution from the metal of the cathode and discharge five cations, and five excess anions lose their extra electrons to the metal of the anode. Thus the current through the two wires is equal, and everything balances from an electrical standpoint.

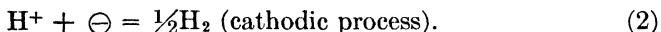
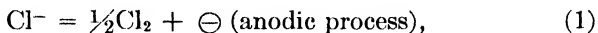
From a chemical standpoint, however, something has happened of great importance. If the conditions are right, the five anions which lose electrons may be five chloride ions, and we have an evolution of chlorine gas (in this case, 2.5 molecules). Under other conditions (cool, dilute solution, and a slow passage of current) five OH^- ions (which are always present in aqueous solution, as well as hydrogen ions) may give up their electrons, forming water and oxygen gas. This satisfies the electrical conditions just as well as the discharge of Cl^- ions; and it is of frequent occurrence that the ions that carry most of the current through the solution are not the ones which are discharged at the electrodes. Thus, in the above case, sodium ions are not usually discharged at the cathode, but hydrogen ions, forming hydrogen gas.¹

The relations are entirely similar when ions are involved whose valence is greater than one, as, for instance, SO_4^{--} . Such an ion transfers twice as much electricity through the solution

¹ It is not a real explanation, that sodium metal is formed and subsequently reacts with water to give hydrogen, as there is no evidence that this takes place, and the formation of NaOH can be explained without this hypothesis, as will be shown.

as Cl^- , for an equal movement; and gives up twice as many electrons at the anode when it is discharged.

61. Electrochemical Processes.—Let us write equations for the electrochemical processes which effect the discharge of chloride and hydrogen ions.



Observe that any anodic process must furnish electrons to be delivered to the wire; any cathodic process must involve the absorption of electrons. Any such equation may be read in two ways. On the small scale, Eq. (1) asserts that one chloride ion is converted into one chlorine atom and one electron. On the large scale, one gram ion (35.458 grams) of chloride ion gives one gram atom of chlorine (or one-half gram molecule) plus one gram equivalent of negative electricity. The gram equivalent of electricity is called the faraday, and has a value of 96,510 coulombs.¹

Movement of the ions through the solution explains how the current is carried through it; electrochemical equations for electrode processes, such as Eqs. (1) and (2), explain how the current gets into and out of the solution. Both parts of the theory taken together are capable of explaining everything of importance that goes on in a cell through which electricity is passed, as they involve Faraday's laws of electrolysis. They express in fact these laws more clearly and exactly than can ordinarily be accomplished through formal statements in words.

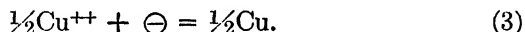
From Eqs. (1) and (2) alone we can see that the solution must become alkaline as the result of electrolysis, as hydrogen ions have been removed (from the water), leaving an excess of hydroxyl ions. For electrical neutrality, these hydroxyl ions must be associated with an equal equivalent weight of some positive ions, in this case, sodium ions. Hence we obtain by the passage

¹ In terms of International (v) coulombs. The value is 96,507 International (a) coulombs, and 96,500 absolute coulombs. In the unlikely event that the student should have to distinguish between values so nearly the same, he may consult "International Critical Tables," Vol. 1. In connection with any experimental work he will probably use the value given in the text above.

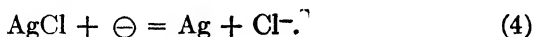
of one faraday of electricity, one-half mole each of hydrogen and chlorine, and one mole of sodium hydroxide. We can see furthermore that the alkalinity is developed around the cathode, as it is here that hydrogen ions are removed from water and discharged.

We cannot however answer the question, either from the equations for the electrode processes or from the hypothesis that metallic sodium is first formed and then decomposes water, whether the sodium necessary for the formation of sodium hydroxide comes from the portion of the solution around the cathode, or from the anodic portion. A little consideration of the movement of the ions shows that each portion furnishes a part of the sodium. From the anode, a certain quantity of sodium ions travels through the solution into the cathodic portion. From the cathode, a certain quantity of chloride ions travels out towards the anode, leaving an equivalent number of sodium ions to be associated with hydroxyl.

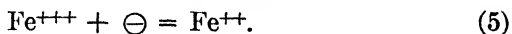
When a solution of copper sulphate is electrolyzed, metallic copper is deposited on the cathode, according to the electrochemical equation



In this case a solid is formed by the discharge of cations instead of a gas. Another type of solid electrode may be made by coating a plate of silver with silver chloride; when this is used as a cathode the following reaction may take place:

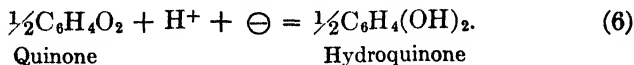


It is not necessary that the discharge of cations (or of anions) should lead to the separation of gas or solid. Thus, if electricity is passed between two plates of platinum or other noble metal immersed in an acid solution of ferrous and ferric chlorides, no precipitation or gas evolution need take place, nor solution of the noble metal. At the cathode the following reaction may occur:



At the anode the reverse process may take place.

An electrode process of considerable interest in connection with the determination of hydrogen-ion concentration is



In the last two cases it is immediately evident that chemical reductions have taken place at the cathode; a ferric salt has been reduced to a ferrous salt, and quinone has been reduced to hydroquinone. Cells in which this immediately obvious type of reduction (and oxidation) takes place are usually called *oxidation-reduction cells*, irrespective of whether a separation of solids takes place or not.

In a broader sense of the words oxidation and reduction, and one quite familiar to every chemist, reduction takes place in every cathodic reaction, and oxidation in every anodic reaction. Thus cupric ion is reduced to metallic copper, and silver chloride to silver, or chlorine to chloride ion. At the cathode, electrons from the wire are absorbed. Any substance that absorbs electrons is reduced. The absorption may be direct, as in the discharge of Cu^{++} , or indirect, as in the case of quinone. The absorption may often be explained in different ways, usually equally well. Thus, in explaining Eq. (6) we may say that the quinone is reduced, or that the hydrogen ion is reduced and simply adds to the quinone, hydrogenating it.

In brief, we have at the cathode, absorption of electrons and reduction; and at the anode, delivery of electrons and oxidation.

There have been given above several electrode processes, mostly written as cathodic reactions. Any cathodic reaction may, however, serve as an example of an anodic reaction, when written or understood in the reverse direction.

In the practical operation of cells it often happens that more than one process occurs at the same electrode. Many variables affect the selection of the particular electrode process which may predominate over other possible processes. Some of these are temperature, pressure (of slight importance except for gases), current density (amperes per unit cross-sectional area of the electrode), kind of electrode material and state of its surface (including any catalytic activity), and concentration of the ions in question. The position of a metal in the electromotive series is of prime importance, and will often determine which metal will be deposited (or dissolved) at an electrode when several possibilities exist. Thus in the case of the following members of this series—sodium, zinc, copper, silver—the tendency of the metal to dissolve (and to remain dissolved) decreases in the

order given. From most solutions of copper and zinc, such as solutions of their sulphates, copper will therefore be deposited at the cathode rather than zinc. In cyanide solutions the effect of concentration of the ions can be of great importance. The tendency of a metal to deposit is greater, the greater the concentration of its ions. In cyanide solutions of copper containing an excess of cyanide there are almost no copper ions, the copper being present as complex anions. From such solutions there is little tendency to deposit. The effect of cyanide on zinc is less, and from a suitable solution zinc and copper may be plated together in the form of brass.

A great many electrode reactions are given in "International Critical Tables."¹ The tendency of the reactions listed to occur as a cathode process (at 25° and under the given conditions of concentration) increases steadily as we pass from lithium down the first table, and as we continue from hydrogen down the second table to the final reaction. Considered as anode processes, the tendency changes in the opposite manner.

Problems

1. (a) A solution of silver nitrate is electrolyzed for 5 min. with a current of 0.5 ampere. How many milligrams of silver are deposited at the cathode? (b) Suppose the current is furnished by two dry cells, connected in series, through an appropriate resistance. The zinc dissolves as Zn^{++} . How many milligrams of zinc are dissolved in each dry cell during the electrolysis?

2. (a) Write the equation of the electrochemical process for the interaction of one electron with water to form hydroxyl ion and hydrogen gas. (b) Write the equation for the decomposition of water into hydrogen ion, oxygen gas, and one electron. In each case, label the reaction as anodic or cathodic. (c) Add the two equations, canceling wherever possible. What information is absent from the result that was present in the two equations?

¹ Vol. 6, pp. 332-333.

CHAPTER XIV

TRANSFERENCE NUMBERS AND THE MOBILITY OF IONS

It was shown in Chap. XII how we can determine from conductance measurements the difference in the equivalent conductances of any two anions at zero concentration, or of any two cations. The method does not enable us to find the difference for two ions of opposite charge. From the study of the movement of ions, when the current is passed, differences of the latter type can, however, be found. Thus, from a study of the transference numbers, by methods to be explained in this chapter, it has been determined that 49.6 per cent of the total current carried by potassium chloride in very dilute solution at 18° is carried by the potassium ion, and 50.4 per cent by the chloride ion. Since the equivalent conductance of potassium chloride at zero concentration is known from conductance measurements to be 129.44, the equivalent conductances at zero concentration can be calculated for potassium and chloride ions, and therefore for many other anions and cations. Tables of equivalent ionic conductances have thus been worked out and are given in the standard reference books.¹ By simple addition, the equivalent conductance at zero concentration can be found for a large number of salts, acids, and bases from the tabulated ionic conductances.

62. The Transference Number.—The transference number of an anion or a cation of an electrolyte is defined to be the fraction of the total current carried by the given kind of ion. The same definition holds, no matter what may be the valence of the ions. The transference number of potassium ion in a solution of K_2SO_4 is the fraction of the total current carried by *all* the K ions (not by half of them). We shall denote the transference number by T , using a subscript to indicate the kind of ion to which it refers. The sum of the transference numbers of all the ions making up the solution is necessarily 1.

¹ For instance, "International Critical Tables," Vol. 6, p. 230, Table 3.

Suppose we pass a current of electricity through a solution of copper sulphate, using copper electrodes, and take note of the effects produced in the solution immediately about the cathode. For every faraday passed, one equivalent (one-half an atomic weight in grams) of metallic copper is deposited on the electrode. If all the current were carried on copper ions, this copper would be entirely replaced by the migration of copper ions towards the cathode. As a matter of fact, only about 0.37 of the current is carried by copper ions—the rest being carried by sulphate ions—and more copper is therefore deposited than is brought up to the cathode, so that the solution about the cathode loses $1 - 0.37 = 0.63$ equivalent of copper per faraday. The number 0.63 is the transference number of the sulphate ion (sometimes called transport number).

If in performing the experiment we do not know the transference number, we can determine it by passing a measured number of coulombs and determining the loss of copper around the cathode. The loss per faraday is then the transference number of the sulphate ion. We must arrange matters so that the variations of density do not stir up the solution. Figure 32 indicates how the electrodes may be arranged.

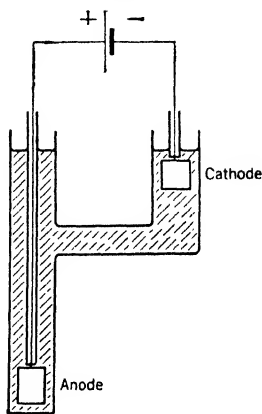


FIG. 32.—Arrangement for measuring transference numbers.

The temperature should be controlled. We analyze the solution before any current is passed to find out how many equivalents of copper are associated with one gram of water. After passing the current, we remove enough of the solution in the right-hand tube to include all of that around the cathode without including any of the anodic portion, and analyze this cathodic portion to find the total number of grams of water and the number of equivalents of copper associated with it. This analysis will involve direct weighing of the solution or a density determination. We can now calculate first the total number of equivalents of copper that would have been associated with the total number of grams of

water, had no current been passed, and then the loss of equivalents due to the passage of the current.

The student will note that the result, which is obtained by a subtraction, is independent of the quantity withdrawn for the analysis, as long as all the cathodic portion, and none of the anodic, is taken.

This loss of equivalents of copper must be divided by the number of faradays passed. This is often determined by passing the same current through a silver coulometer (by connecting it in series with the cell to be studied) and weighing the silver deposited. In the present case we might simply weigh the copper cathode before and after the electrolysis; by dividing the increase of weight in grams by $\frac{1}{2}$ of 63.57 we should obtain the number of equivalents of copper deposited, which equals the number of faradays passed through the solution.

Division of the loss of equivalents of copper by the number of faradays passed gives $1 - T_{\text{Cu}}$ or the transference number of the sulphate ion.

In this case we might determine also the gain of copper about the anode. Since, per faraday, one equivalent of copper dissolves and only T_{Cu} equivalents migrate away towards the cathode, the gain per faraday is $1 - T_{\text{Cu}}$ equivalents, the same as the loss at the cathode. In such an event it is customary to withdraw also a middle portion; this should not experience any change of copper-ion concentration.

The procedure described above, in which the change of copper-ion content is determined with reference to the water associated with the copper ion, is the ordinary, or Hittorf, transference number.

63. The Gain or Loss Table.—It is instructive to consider the sum total of all effects in the solution due to the passage of one faraday through the cell. This is best done by means of some sort of balance sheet, such as the gain table shown in Table I on page 113.

The net effects in the solution may also be described as a net gain of T_{SO_4} equivalents of CuSO_4 at the anode, with an equal loss at the cathode. Besides these effects in the solution, one equivalent of copper was dissolved from the anode, and an equal quantity deposited on the cathode.

TABLE I.—GAIN TABLE FOR THE PASSAGE OF ONE FARADAY THROUGH A COPPER SULPHATE SOLUTION BETWEEN COPPER ELECTRODES

At the anode		At the cathode	
Gain through electrode process	Gain through migration	Gain through electrode process	Gain through migration
1 eq. Cu^{++}	$-\text{T}_{\text{Cu}}$ eq. Cu^{++} $+\text{T}_{\text{SO}_4}$ eq. SO_4^{--}	-1 eq. Cu^{++}	T_{Cu} eq. Cu^{++} $-\text{T}_{\text{SO}_4}$ eq. SO_4^{--}
Net gain of Cu^{++} = $1 - \text{T}_{\text{Cu}} = \text{T}_{\text{SO}_4}$ eq.		Net loss of Cu^{++} = $1 - \text{T}_{\text{Cu}} = \text{T}_{\text{SO}_4}$ eq.	
Net gain of $\text{SO}_4^{--} = \text{T}_{\text{SO}_4}$ eq.		Net loss of $\text{SO}_4^{--} = \text{T}_{\text{SO}_4}$ eq.	

It is not difficult to construct a similar gain table for the electrolysis of other solutions. If water is decomposed, as when a dilute solution of acid is electrolyzed, the loss of water should be entered in the table. In such a case the actual calculation of the transference numbers from the analysis is a little more complicated, since the loss of water alone changes the ratio of weight of ion in question to the weight of water associated with the ion, and this must be taken into account.¹

64. Complex Ions.—The transference number of a given kind of ion can be clearly discussed when we know what kinds of ion are present in the solution. When we do not know this, we can gain much information through transference experiments. Suppose we are interested in potassium silver cyanide, the formula of which is often given as $\text{AgCN} \cdot \text{KCN}$. In a study of transference numbers we should naturally study the migration of the components Ag, CN, and K. The silver and cyanogen are found to move towards the anode, and the potassium towards the cathode like any positive ion. When the cathode portion is studied, and account is taken of the loss of silver due to deposition on the cathode, the numbers of equivalents of these compo-

¹ For this, two equations will be found available, involving two unknowns: the transference number, and the number of grams of unchanged solution which the sample includes. The two equations express the weights of electrolyte, and of water, respectively, in the sample taken for analysis after the electrolysis.

nents migrating per faraday are found to be about 0.40, 0.80, and 0.60 for Ag, CN, and K, respectively. The sum exceeds unity, showing that more than one component must be present in some ion. The numbers 0.40 and 0.80, together with the fact that both Ag and CN move with the anions, suggest the presence of the single kind of anion $\text{Ag}(\text{CN})_2^-$. Supposing that the ions principally present are really K^+ and the complex ion $\text{Ag}(\text{CN})_2^-$, we find their transference numbers to be 0.60 and 0.40, respectively. They sum up to unity, and the value 0.40, applied to the symbol $\text{Ag}(\text{CN})_2^-$, shows that 0.40 equivalent of Ag and 0.80 of CN migrate per faraday. A better formula for the substance is therefore $\text{KAg}(\text{CN})_2$, as it more nearly suggests the manner in which it is ionized in water solution to $\text{K}^+ + \text{Ag}(\text{CN})_2^-$. The same method has been applied to establish the nature of other complex ions.

In the above case there are few positive silver ions in the solution, but sufficient so that silver is deposited at the cathode, in accordance with the cathode reaction



No silver is deposited at the anode, in fact silver anodes are used in silver plating from such solutions in order to maintain the strength of the bath in silver, in which case the silver anode dissolves under the action of the current.

Just as we have sometimes more than one component in an ion, so do we sometimes have the same substance present as a component of more than one ion. The transference number of cadmium is reported as negative in strong solutions of cadmium iodide. This is because cadmium is assumed to be a cation in the computation, whereas it is present also in a negative complex ion, and in strong solutions more cadmium is carried as anion than as cation.

65. The Mobility of Ions.—We have already referred to the speed of two ions, as being equal or unequal, when both ions were under the same electrical influence. It is now convenient to specify unit conditions of electrical influence. This will enable us to define the mobility of an ion as its speed under unit conditions.

We expect of an ion moving in a viscous medium under the influence of an electrical field that its speed will not build up indefinitely with time, like the speed of a freely falling body, but that it will acquire a constant velocity, proportional to the so-called potential gradient. This is, when the conditions are uniform, the voltage drop between the electrodes, divided by the distance in centimeters between them. Let the velocity of the ion be denoted by V , when the distance between the electrodes is l , and the drop of voltage between them is E volts. Then V is proportional to E/l , or

$$V = UE/l \quad (1)$$

The factor of proportionality U is called the mobility of the ion, and is equal to the velocity of the ion when the potential gradient E/l is unity.

The number of coulombs carried by a gram equivalent of ions, 96,510, the value of a faraday, we shall represent by F . Let us consider two parallel plates 1 cm. apart containing a solution in which there is one gram equivalent each of cations and anions. The conductance due to anions would be called the equivalent conductance of the anions (Chap. XII, page 93) and will be designated by Λ_{a-} . That due to cations will be the equivalent conductance of the cations Λ_{c+} . Suppose there is a voltage drop of one volt between the plates. Then, if it were possible for all the anions (one gram equivalent) to move 1 cm. in 1 sec., the current thus carried would be F coulombs per second. Since, however, the anions move with a velocity of U_{a-} cm. per second (since the potential gradient is unity), the current actually carried by the anions is only FU_{a-} (*only*, because the mobility is a small fraction). Since the voltage drop between the plates is one volt, the conductance equals the current.* Hence

$$\Lambda_{a-} = FU_{a-} \quad (2)$$

and, similarly for the cations,

$$\Lambda_{c+} = FU_{c+}. \quad (3)$$

The total equivalent conductance of the electrolyte which is 100 per cent ionized is the sum

$$\Lambda_0 = \Lambda_{a-} + \Lambda_{c+} = F(U_{a-} + U_{c+}). \quad (4)$$

* $I = E/R$ by Ohm's law. When $E = 1$, $I = 1/R$.

We add the subscript zero to the first lambda because we have assumed 100 per cent ionization, which we cannot always expect except at zero concentration.

Suppose we have between the plates one gram equivalent of an *electrolyte* which is not 100 per cent ionized, the degree of ionization being given by the fraction α . Then the equivalent conductance of the *electrolyte* will be α times the value given above in Eq. (4), that is,

$$\Lambda = \alpha\Lambda_{a-} + \alpha\Lambda_{c+} = F(\alpha U_{a-} + \alpha U_{c+}). \quad (5)$$

If the mobilities are the same in some strong solution whose equivalent conductance is Λ , as in the infinitely diluted solution whose equivalent conductance is Λ_0 , the degree of ionization α will be equal to the conductance ratio Λ/Λ_0 . This appears at once on performing the division by means of Eqs. (4) and (5):

$$\frac{\Lambda}{\Lambda_0} = \alpha \frac{U_{a-} + U_{c+}}{U_{a-} + U_{c+}}. \quad (6)$$

The right-hand side reduces to α , provided that the mobilities in the numerator are equal to those in the denominator.

A simple relation exists between the equivalent conductances of the ions and the transference number and likewise between the mobilities and the transference number. The fraction of the current carried by the anion is

$$T_a = \frac{\alpha\Lambda_{a-}}{\alpha(\Lambda_{a-} + \Lambda_{c+})} = \frac{F\alpha U_{a-}}{F\alpha(U_{a-} + U_{c+})}. \quad (7)$$

$$\text{Hence, } T_a = \frac{\Lambda_{a-}}{\Lambda_{a-} + \Lambda_{c+}} = \frac{U_{a-}}{U_{a-} + U_{c+}}. \quad (8)$$

Similar equations hold for the cation. From Eqs. (5) and (7) we have also

$$T_a = \alpha\Lambda_{a-}/\Lambda \quad (9)$$

where Λ is the equivalent conductance of a solution containing one gram equivalent of electrolyte per liter. This may be applied to an infinitely dilute solution, in which α is unity, giving the equation

$$\Lambda_{a-} = T_a\Lambda_0. \quad (10)$$

In this case, Λ_{a-} is the limiting equivalent conductance of the

anion, and Λ_0 that of the electrolyte. T_a is the transference number of the anion in the infinitely dilute solution.

The transference numbers of potassium chloride solutions do not change very rapidly with the concentration, and the value of T_a can be estimated for potassium chloride at zero concentration. From this one transference number and the limiting equivalent conductances of the electrolytes, the equivalent conductances at zero concentration have been calculated for a whole series of anions and cations by the use of Eq. (10) and the corresponding equation for the cation:

$$\Lambda_{c+} = T_c \Lambda_0 = (1 - T_a) \Lambda_0. \quad (11)$$

The limiting ionic conductances of hydrogen and hydroxyl ions are unusually high, being 315.2 and 173.8, respectively, at 18°. The mobility of the hydrogen ion is 315.2/96510, or about 0.00327 cm. per second and per unit potential gradient in volts per centimeter. By applying a potential difference of 110 volts across a short distance of a few centimeters between electrodes, the hydrogen ions in an acid solution will be caused to travel an appreciable distance in 1 min. Such a motion has been directly observed by passing a current through a cell in which there is a stratum containing a dilute solution of a strong acid, next to a stratum containing a salt of the acid (to give some conductivity to this stratum) together with some phenolphthalein colored red with a trace of alkali. For convenience of qualitative demonstration, jellies containing agar-agar may be used, the strata being introduced into the apparatus while liquid, and the first being permitted to freeze before the addition of the second.¹ On passing the current in the proper direction, the hydrogen ions migrate into the phenolphthalein stratum and decolorize it.

It is possible to determine transference numbers by measuring the velocity with which the boundary between two solutions moves under measured electrical conditions, or by observing the motion of two boundaries in the same time. This is called the moving boundary method.² As will be seen under the next

¹ NOYES and BLANCHARD, *Z. physik. Chem.*, **36**, 1 (1901).

² A good description of the method, with a discussion of some necessary experimental refinements, is given by MacInnes and Smith, *J. Am. Chem. Soc.*, **45**, 2246 (1923). See also MacInnes and Cowperthwaite, *Proc. Nat. Acad. Sci.*, **15**, 18 (1929).

heading, the velocity with which the boundary moves is not the same as the velocity of the ion in the solution on one side of the boundary, unless the electrolyte furnishing the ion is completely ionized.

It has been found that the transference numbers of strong electrolytes depend somewhat upon the concentration, as well as on the temperature. This variation with concentration is one of the facts which has led to the belief that the conductance ratio is not equal to the degree of ionization in the case of strong electrolytes. For if the transference number, equal to $U_{a-}/(U_{a-} + U_{c+})$, varies with the concentration, so must the mobility U_{a-} , and it is only when the mobility is independent of the concentration that we may explain the variation of equivalent conductance with concentration as due solely to a variation in the degree of ionization.

66. Equivalent Conductance and Mobility of an Ion-constituent.—In the discussion of many relations in which concentrations are concerned, it is necessary to distinguish the ion from the ion-constituent. The ion-constituent is that part of an electrolyte which includes the ions of one kind already present, together with the ions of this kind that would be present, were the ionization in question 100 per cent complete. Thus, acetic acid may be regarded as composed of hydrogen ion-constituent and acetate ion-constituent. If the strength of the acetic acid is one molal, the strength of the hydrogen ion-constituent is also one molal, as well as that of the acetate ion-constituent; the molality of hydrogen ions and of acetate ions is very much smaller.

It is the concentration of hydrogen ion-constituent that is determined in the titration of a weak acid by a standard solution of a (strong) base; not the concentration of ions. The reason is obvious. In the solution of weak acid only a fraction of the ion-constituent is actually present in the form of ions, but as hydrogen ions are removed by addition of base, according to the equation $H^+ + OH^- = H_2O$, more are formed by ionization according to an equation such as $HAc = H^+ + Ac^-$, so that all of the hydrogen ion-constituent can be used up by titration to a proper endpoint.

The equivalent conductance of an electrolyte refers to one gram equivalent of electrolyte between the plates of the cell. By Eq. (5) it is equal to

$$\alpha\Lambda_{a-} + \alpha\Lambda_{c+},$$

where Λ_{a-} and Λ_{c+} refer to one gram equivalent of ions between the plates. The part of the equivalent conductance of the electrolyte due to the anion-constituent is $\alpha\Lambda_{a-}$ and is called the equivalent conductance of the anion-constituent, designated by Λ_a , without the minus sign over the a . The part of the equivalent conductance due to the cation is similarly $\alpha\Lambda_{c+}$ and is designated by Λ_c . We have then

$$\Lambda_a = \alpha\Lambda_{a-},$$

$$\Lambda_c = \alpha\Lambda_{c+},$$

and

$$\Lambda = \Lambda_a + \Lambda_c. \quad (12)$$

The transference number can be related to the equivalent conductances of the ion-constituents; indeed, from Eq. (7) we have

$$T_a = \frac{\Lambda_a}{\Lambda_a + \Lambda_c} = \frac{\Lambda_a}{\Lambda}. \quad (13)$$

Similarly, if we call αU_{a-} the mobility of the anion-constituent, and represent it by U_a , and do the same for the cation, we shall have from Eq. (7)

$$T_a = \frac{U_a}{U_a + U_c}. \quad (14)$$

The transference number is given by entirely similar expressions [Eq. (8) compared with Eqs. (13) and (14)], whether we deal with the equivalent conductance and mobility of the ion or of the ion-constituent. There is no distinction between the transference number of an ion and of the ion-constituent to be seen according to the theory, but since we determine by analysis the ion-constituent, rather than the ions, some prefer always to speak of the transference number of the ion-constituent.

Returning to the motion of a boundary between an acid solution and a solution containing a salt of the acid and some

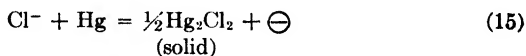
phenolphthalein, let us consider the case in which the acid is slightly ionized. The hydrogen ions will move ahead of the boundary and penetrate into the salt solution, there to combine mostly with anions of the salt to form undissociated acid. Those that survive for a short distance will soon be lost on further migration. The imaginary boundary of the foremost hydrogen ions cannot therefore be observed. The movement of a real boundary will be determined by the velocity with which a layer of hydrogen ions, having as many hydrogen ions per liter as the original solution, moves forward. If under unit potential gradient only the fraction α of the acid consists of migrating hydrogen ions with the mobility U_{H^+} , the velocity of the real boundary will be only αU_{H^+} . This is what was called above the mobility of the ion-constituent U_H , and this fact is a very good reason for so doing.

In a good moving boundary experiment the electrical current would actually be passed in the opposite direction, causing the hydrogen ions to retreat from the salt solution. In this case it is quite easy to see that to move the boundary of the retreating acid it is necessary to move all of the hydrogen ion-constituent.

The mobility that can be measured by direct observation without knowing the degree of ionization is the mobility of the ion-constituent.

Problems

1. A solution of KCl is electrolyzed between two similar electrodes consisting of mercury in intimate contact with mercurous chloride, Hg_2Cl_2 . The electrochemical reaction is at one electrode



and is the reverse at the other electrode. Construct a gain table after the pattern of Table I, showing the effects in the solution per faraday. Give a sketch, placing the anode at the left, and proceed systematically. We shall always imagine the (positive) current to pass through the cell from left to right.

2. Calculate how many centimeters the hydrogen ions will move in 1 min. when a potential of 110 volts is applied over a distance of 5.5 cm. in a * dilute aqueous solution of a strong acid at 18°.

3. Consider a 0.1 normal solution of a weak acid which is 1 per cent ionized. (a) What is the normality of the hydrogen ions; (b) of the hydrogen ion-constituent?

CHAPTER XV

THERMODYNAMICS AND FREE ENERGY

To an ever increasing extent, biologists are using the results and language of thermodynamics. For many purposes it is quite unnecessary to understand the formal development of thermodynamics into a logical science; many of the results can be understood and applied by anyone after a brief explanation of the language in which they are expressed. Of the various functions discussed in works on thermodynamics, such as the energy, entropy, heat function, etc., we shall use here only the so-called free energy, and shall be able to explain by its use the electromotive force of cells, the law of mass action, and the important Donnan equilibrium.

67. The Change of State.—A most important concept of thermodynamics is the change of state. We shall continue to regard the state as being fixed by the temperature, pressure, and composition, as in Chap. I. Let a system¹ be initially in a state *A*, characterized by certain definite values of the temperature, pressure, and composition (qualitative as well as quantitative), and let the system undergo a change to a final state *B*, characterized by certain values, some of which are not the same as before. Then the change of state is simply the change from state *A* to state *B*. It is completely defined by describing fully the states *A* and *B*, and has no reference whatever to the particular series of intermediate states through which the system may have passed on its way from *A* to *B*, nor to the nature of the process by which the changes are effected.

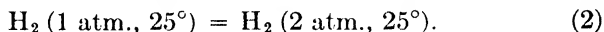
A change of state of aggregation, such as solid to liquid, is one example. Such a change may be given as an equation



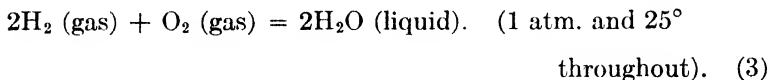
¹ A system is a body, or a substance, or a collection of bodies or substances considered collectively for purposes of discussion.

which will be read from left to right. The symbol H_2O will be taken to represent one mole of water for definiteness in discussing changes of free energy. As regards the state itself, the state of one mole of ice at 1 atm. and 0°C . is the same as the state of any other quantity at the same pressure and temperature.

Another simple example of a change of state (that does not this time involve a change in the "state of aggregation") is

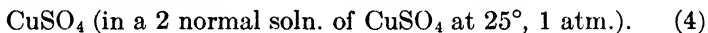


Another example, in which the pressure and temperature are both constant:



Any chemical equation defines a change of state if the temperatures and pressures are specified; the temperatures and pressures do not necessarily have to be the same throughout.

Sometimes we have to consider a change of state of the type CuSO_4 (in a normal soln. of CuSO_4 at 25° , 1 atm.) =



In this change of state there is a *transfer* (not necessarily by electrical migration or *transference*) of one mole of copper sulphate from one solution to another, without a change of temperature or pressure, and without an appreciable change of composition of the two solutions. We will suppose that the transfer is from a very large quantity of one solution to a very large quantity of the other, so that the strengths of the two solutions are not appreciably altered by the transfer. Note that if the two solutions were of the same strength, there would here be no change of state, as the mere difference of location does not affect the state.

68. The Maximum or Reversible Work.—In general we can obtain work from a system which is spontaneously undergoing a change of state, but the amount of work depends on the carefulness with which we avoid losses of work due to friction, etc., and often depends also on the series of intermediate states through which the system is passing. In the special case of changes of

state conducted throughout at constant temperature, it is proved in thermodynamics that the nature of the intermediate states is of no importance; but the amount of work actually obtained will still depend greatly on the carefulness with which losses are prevented. The maximum quantity of work will be obtained when there is no waste of work through friction or unbalance of forces or of tendencies of substances to diffuse or to react chemically. This maximum work may be called the reversible work, for if all the forces and tendencies are balanced, it will be possible by very slightly altering the balance to reverse the direction of the change of state, and the same amount of work will then be absorbed by the system in the reverse change B to A as was delivered by the system in the direct change A to B . It will be recognized that if the forces are absolutely balanced, nothing can happen at all. The maximum work is the ideal limit to which we may theoretically approach by more and more completely perfecting the balance (and thus making the process slower and slower).

69. The Free Energy of Helmholtz.—Because in changes at constant temperature the nature of the intermediate steps is of no importance, there is a definite capacity of a system for doing work in constant-temperature changes of state, which capacity is known as the free energy of Helmholtz, or as the “work content.”¹ The decrease in this capacity is measured by the maximum quantity of work obtainable in the change of state when conducted throughout at constant temperature.

70. The Free Energy.—When a change of state occurs at constant pressure, work may be done in the expansion of the system against the external pressure. It is proved that its magnitude will be given by the product of the pressure times the increase of volume (and will be negative, if the volume decreases). This work against constant external pressure depends evidently on the initial and final states alone. Hence, since there is a definite capacity of the system for doing work in constant temperature changes of state, there must be, in the case of changes of state at both constant temperature and constant pressure, a definite capacity of the system for doing work *in*

¹ There are other names. Every name is misleading, if supposed to be self-explanatory.

excess of the work of expansion. This latter capacity is known in America, and to an increasing extent elsewhere, as simply the free energy.¹

If the system consists of several parts at different pressures, constant pressure implies that each pressure is constant, and the work of expansion is the algebraic sum of all the works of expansion.

The decrease of free energy attending a change of state at constant temperature and pressure equals the maximum work obtainable from the change when this is conducted throughout at constant temperature and pressure, but without including the work of expansion or compression. If the change of free energy considered is an increase, the increase equals the least work that must be expended on the system, without including any work of expansion or compression. In processes that proceed spontaneously when the temperature and pressure are held constant, it is proved that the change of free energy attending the spontaneous process must be a decrease.

In electrical cells, the decrease of free energy attending the chemical and physical changes equals the maximum amount of electrical work theoretically obtainable from the cell when operated, as is ordinarily the case in practice, at constant temperature and pressure. This is because the *only* work obtainable from a theoretically good cell is electrical work and the work of expansion.

The total free energy of a system consisting of a number of distinct bodies or phases equals the sum of their free energies. The total free energy of a solution can be expressed as the sum of the partial free energies of the various components, and each of these partial free energies can be expressed as the partial molal free energy of the component in the solution times the number of moles of the component in the solution.

71. Chemical Equilibrium.—From a chemical standpoint, electrical cells are not strictly in equilibrium. An ordinary dry

¹ This is due to the influence of G. N. Lewis, who applied this name to the *zeta* function of Gibbs, after pointing out the inconvenience of the free energy of Helmholtz, as applied by European writers to the ordinary chemical problem, which is usually stated with reference to temperature and pressure.

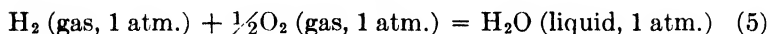
cell has a limited "shelf life." There is a tendency for certain chemical reactions to take place. We obtain an electrical cell by so arranging matters that the direct chemical process is slow and difficult, whereas the chemical reaction can easily and quickly take place by means of electrochemical processes. Whenever any chemical or physical process is taking place spontaneously there are active forces or tendencies in play; whether they are electrical or not, we may imagine ourselves able to oppose the forces or tendencies, thus slowing up the process and forcing the system to do work for us in undergoing the change of state. If, however, a system is in equilibrium¹ there will be no such active forces or tendencies, other than the natural tendency of the system as a whole to expand against the external pressure. Consequently, if a change of state is conducted at constant temperature and pressure no work can be done by the system, other than the work of expansion, provided the system is in chemical equilibrium, and the corresponding change of free energy will be zero for such a change. This proposition will enable us easily to deduce the law of mass action for equilibrium (Chap. XX).

72. The Energy.—The free energy is not the same as the energy of a system. This represents the capacity of the system for doing work and furnishing heat, and the change of energy gives the combined amounts of work and heat, without any information about the work or heat separately. There is in fact no function of thermodynamics, the change of which, as determined by simple subtraction, gives either the work or heat separately in a general manner; that is, without reference to restrictions such as constant temperature, reversible operation, and the like. The energy will be discussed again in Chap. XXVII.

73. The Free Energy of a Substance.—If a system of substances undergoes a chemical reaction with a loss of free energy, we can evidently interpret this by saying that the free energy of the products of the reaction is less than that of the substances

¹ We exclude from consideration here false or apparent equilibrium, secured not by a balance of active forces, but rather by delays such as those due to the viscosity of fluids, or to the "passive resistances" discussed by Gibbs, which are analogous to the friction that keeps a body from sliding down a slightly inclined plane.

consumed in the reaction. By a suitable choice of chemical reactions it is possible to gain more definiteness. It has been found that the loss of free energy in the reaction



at 25° is 56,560 cal. In order to establish a system of reporting free energies it is agreed that the free energies of all pure elements shall be considered zero at the standard temperature and pressure (25° and 1 atm.) and in the state of aggregation or crystalline form in which they are stable. Accordingly, the free energy of one mole of liquid water at 1 atm. and 25° is -56,560 cal.¹

By means of the convention, that the free energy of all pure elements shall be considered zero when in their standard states, it is possible in principle to find a value of the free energy for a mole of any substance. Hence we are at liberty to discuss the free energy of a substance, whether or not the numerical value has actually been determined.

When one substance is dissolved in another there is a change of state and a corresponding change of free energy. We shall now consider how to imagine the free energy of a solution to be divided among the components of the solution.

74. The Partial Molal Free Energy of a Substance.—If we consider a pure substance, the free energy of a mole of the substance is simply the free energy of the total quantity of the substance divided by the number of moles in the quantity. But if we consider a solution, we cannot find the free energy of a mole of a substance in it by any such division. For the components of the solution will not have the same free energy per mole (even in the pure state), and therefore we cannot calculate the free energy of a mole of one substance from the total free energy and the numbers of moles present. Gibbs showed that the partial molal free energy of a substance 1 may be defined as the increase in the total free energy of the solution, when a very small number of moles dn_1 is added to the solution at constant temperature and pressure, divided by dn_1 . Let F be the free

¹ The loss of free energy is 56,560 cal., which means that this much free energy has been taken from a system which before the reaction had none. Hence the free energy of the liquid water is less than zero; *i. e.*, -56,560 cal. per mole.

energy of the solution, dF its increase when dn_1 moles are added, and \bar{F}_1 the partial molal free energy of substance 1, then the definition is

$$\bar{F}_1 = dF/dn_1 \text{ (at constant } T \text{ and } p \text{ and without adding other substance)}. \quad (6)$$

He showed that the sum of the partial molal free energies, each multiplied by the number of moles present, equals the total free energy of the solution:

$$F = \bar{F}_1 n_1 + \bar{F}_2 n_2 + \bar{F}_3 n_3 + \text{etc.} \quad (7)^1$$

What we call the partial molal free energy was called by Gibbs the chemical potential and denoted by a Greek μ .² For a pure substance, \bar{F}_1 equals simply F/n_1 , or the partial molal free energy of a pure substance equals its free energy per mole.

75. Equilibrium and the Partial Molal Free Energy.—Consider two solutions, not identical in composition, in separate vessels but at the same pressure and temperature. Imagine that each solution is present in large quantity, so that a mole of substance 1 may be removed from the first solution and added to the second without perceptibly altering the concentrations of the solutions. Then the decrease of free energy of the two solutions, considered as one system, will be the difference of the partial molal free energies of substance 1 in the two solutions $\bar{F}_1' - \bar{F}_1''$. For \bar{F}_1' represents the loss of free energy of the first solution, when a mole of substance is removed from it, and \bar{F}_1'' represents the gain of the second solution, when a mole is added to it.³

¹ Equation (7) cannot be derived from Eq. (6) without recognizing that \bar{F}_1 is independent of the total mass, so long as the temperature, pressure, and the composition are constant.

² Many authors follow G. N. Lewis rather than Gibbs, and call it the partial molal free energy, *partial* referring to the fact that the derivative of Eq. (6) is a partial derivative. They denote it by \bar{F}_1 , as above. Gibbs defines the chemical potential first with reference to the energy (together with entropy and volume) and later with reference to free energy (together with temperature and pressure).

³ The condition of substance 1 is changed when its environment is thus changed, and naturally also its free energy. The change of free energy of the system may be thought of as the difference of free energy of the substance 1 in the two solutions because of the difference in its condition. The definition of \bar{F}_1 is such that we get the right answer without considering the effect of substance 1 on the other substances present in the solutions.

If now the two solutions, at the same temperature and pressure, are also in equilibrium with respect to transfer of substance 1, then $\bar{F}_1' - \bar{F}_1''$ must equal zero, as the change of free energy is zero when the system is in equilibrium and the change is conducted at constant temperature and pressure. That is, at equilibrium the partial molal free energy of substance 1 is the same in both phases. Gibbs showed that this is true whenever different phases are in equilibrium and not under the influence of gravity, electricity, or other special forces.¹

If, again, the two solutions, at the same temperature and pressure, are not in equilibrium with respect to transfer of substance 1, it may be possible to arrange an electrical cell by means of which the substance may be transferred from one solution to the other reversibly (that is, without wasting any of the capacity of the system for doing work) at constant temperature and pressure. In this case the difference of the partial molal free energies, $\bar{F}_1' - \bar{F}_1''$, representing the loss of free energy of the two solutions, must be equal to the electrical work the system can do per mole of substance 1 transferred. This principle will enable us to obtain formulas for the electromotive force of "concentration cells."

76. The Effect of Pressure and Concentration on the Free Energy.—Gibbs showed that the rate of change of the free energy of a mole of any pure substance with pressure at constant temperature is equal to its molal volume. In symbols, let \bar{F} be the free energy of a mole, then

$$(d\bar{F}/dp) = v \text{ (at constant temperature).} \quad (8)$$

When the substance is a gas following the ideal gas law, $v = RT/p$ and

$$d\bar{F} = RTdp/p \text{ (at constant temperature).} \quad (9)$$

At constant temperature this can be integrated, giving

$$\bar{F} = RT \ln p + I, \quad (10)$$

¹ The components may be in chemical equilibrium. Sometimes the transfer of substance at constant temperature would necessitate either a change of pressure or a departure from a condition of equilibrium, in which case our proof is not complete, but that of Gibbs is.

where the integration constant I depends only on the temperature and kind of gas. This result is given by Gibbs and may be accepted by students lacking confidence in their integrations. It furnishes a good starting point for discussing later the mass action law for gases.

Turning now to solutions of the gas in a solvent, such as water, we can easily find an expression for the partial molal free energy of dissolved gas, provided the solution follows Henry's law. For in such a case

$$p = k'x_1,$$

or, for dilute solutions,

$$p = k''c,$$

where c is the concentration of the dissolved gas in moles per liter of solution. Hence,

$$\bar{F} = RT \ln (k''c) + I = RT \ln c + RT \ln k'' + I. \quad (11)$$

At constant temperature and pressure $RT \ln k'' + I$ is constant and may be simply denoted by the letter k .¹ The partial molal free energy of dissolved gas in the solution is the same as that in the gas phase, since the phases are supposed in equilibrium, and is given therefore by

$$\bar{F} = RT \ln c + k. \quad (12)$$

The constant k will be different for different substances even at the same temperature and pressure.

For the solvent in a dilute solution it is well to keep to the mole fraction and write

$$\bar{F} = RT \ln x + k, \quad (13)$$

where all the symbols refer to the solvent.

Equations (10), (12), and (13) make it possible to apply the general theory to numerical calculations.

¹ We must admit that k may vary with the pressure, since we do not wish to limit ourselves to the case in which the solution is always under the vapor pressure of the dissolved gas.

Problems

None of these involves any consideration of the kind of units in which the energy, free energy, or work is expressed.

1. The heat of combustion of coal is measured in a (constant volume) bomb calorimeter. (a) Is the heat evolution equal to the loss of energy; (b) to the loss of free energy?

2. A storage cell is very slowly discharged at constant temperature and pressure. (a) Is the electrical work done equal to the loss of energy; (b) to the loss of free energy? (c) Under what conditions might the loss of free energy exceed the loss of energy when an electrical cell is discharged slowly at constant temperature and pressure?

3. Show that the partial molal free energy of gas 1 in a gas mixture is $RT \ln (px_1) + I$, where p is the pressure of the mixture and x_1 is the mole fraction of the gas in the mixture. Consider pure gas 1 at such a pressure that it will be in equilibrium with the mixture through a semipermeable membrane, and use the simple theory of gases and of gas mixtures (Chap. II).

CHAPTER XVI

ELECTROMOTIVE FORCE AND FREE ENERGY

Let us return to the consideration of the cell, discussed in Chap. XIV, in which copper sulphate solution is electrolyzed between copper electrodes. The cell may be arranged as in Fig. 33, so as to utilize gravity in keeping the solutions separate. If we continue to pass current as indicated, the solution about the anode at the bottom will become stronger, and that about the cathode at the top weaker, than the original solution. Let us pass the current until a considerable difference of concentration

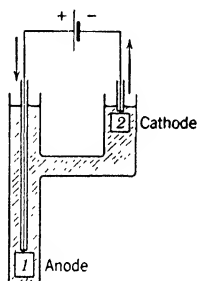


FIG. 33.—Difference of concentration produced by electrolysis.

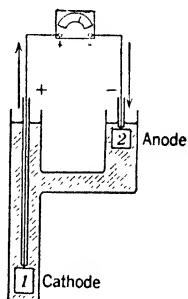


FIG. 34.—Electrical current produced by difference of concentration.

is produced. There is now a tendency for the difference of concentration to be equalized. If we discontinue the charging current and let the apparatus stand, the difference of concentration will gradually be obliterated by diffusion of copper sulphate from the strong to the weak solution.

77. A Simple Concentration Cell.—Such a difference of concentration may, however, be equalized in a more interesting manner. If, namely, the copper electrodes be connected electrically with a voltmeter in series, a current will flow as indicated in Fig. 34. Copper will be dissolved from electrode 2, upon which

it was deposited, and will be deposited now on electrode 1. The current flow is opposite in direction to that of the original charging current, the transference of ions is opposite, and the net effect per faraday is the transfer of T_{so_4} equivalents of CuSO_4 from the strong to the weak solution. The electrodes have furthermore exchanged their functions as anode and cathode, and an electrician would name the polarities of the wires connected to them as shown in Fig. 34.

The system acts like a storage battery but is of the simplest possible type, since only one kind of metal is used, and only one electrochemical process. It is a "concentration cell." If the reading of the voltmeter is noted from time to time it will be found that the terminal voltage decreases as the concentrations approach each other in value, and finally falls to zero. In order to find the greatest terminal voltage which the cell produces at a given time it will be necessary to use a sensitive voltmeter of very high resistance, so that the cell will not perceptibly alter during the measurement. The value of the terminal voltage is in fact greatest when no current is flowing. This maximum value is called the electromotive force of the cell. It can be measured by means of a potentiometer, which, when properly used, draws on the average no current from the cell. The principle of the potentiometer (not to be confused with a term in popular radio parlance) will be described later.

The above cell is not very practical as a storage cell, partly because of the difficulty in keeping the solutions separate, and partly because the electromotive force varies greatly in the discharge.

78. The Principle of Electromotive Force Calculations.—From a free energy standpoint, the free energy of the system was increased when the current was passed through it (by an amount equal to the electrical work done upon it, in the limiting case of very slow and efficient operation at constant temperature and pressure), and in the discharge, the free energy decreases again, permitting us to gain an equal amount of electrical work (again, in the limiting case).

As the current was passed through the cell the electromotive force increased because of the progressive changes of concentration. In order to find the electromotive force when the concen-

trations have certain definite values, we are going to imagine that a faraday of electricity is passed through the cell, but that *the concentrations are not perceptibly changed*. This will be the case when there is a very great amount of each solution present in the cell. There is no objection to considering the amounts of the solutions as great as we please, since the electromotive force does not depend on the size of the electrodes nor on the quantities of the solutions.¹ And when the electromotive force is measured, as little current as possible will be drawn from the cell, in order not to change the concentrations and thus the electromotive force.

Whenever in later sections of the book we speak of passing one faraday through a cell, it must always be understood that this is imagined to be accomplished without perceptibly changing any concentrations.

We obtain useful formulas for the electromotive force of cells by (1) imagining one faraday passed through the cell, always passing positive current through the cell from left to right, and without changing the concentrations, (2) computing the loss of free energy of the cell due to the passage of one faraday, and (3) putting the electrical work done when the faraday is passed equal to the corresponding loss of free energy.

79. The Conventional Representation of Cells.—Let us write a formula for the copper concentration cell discussed above, as follows:



A single vertical line indicates a boundary between two phases, a strong and a weak solution being considered as two different phases.² A convention is widely observed, and is here recommended, for the sign of the electromotive force of cells. The electromotive force is considered positive if on connecting the electrodes by a wire the positive ions move from left to right through the cell as written in the cell formula, such as formula

¹ The electromotive force of a flash-light cell is as great as that of a No. 6 dry cell, though the terminal voltages will differ if a large current is drawn from each.

² We do not apply the ordinary phase rule to electrical cells, or to any systems in which electrical forces interfere with chemical equilibrium.

(1). An electrician would then call a wire leading from the right-hand electrode the positive terminal or pole.

The sign of the electromotive force of the above cell, as written, is positive. For, the equalization of the concentrations does not occur through a mere migration of Cu ions from one solution to the other, but by a combination of ionic migration and electrode processes. If in the above cell we pass current through the cell from left to right, more copper is plated out at the cathode at the right than is brought up by migration of copper ions, so that, when everything is summed up, copper sulphate is transferred from the strong solution to the weak one. This is what naturally happens when, instead of our passing the current arbitrarily from left to right, we merely connect the electrodes and let the current pass as it will; consequently the electromotive force of the cell as written is positive. If it is written reversely, the sign becomes negative.

80. The Calculation of an Electromotive Force.—We may apply Eq. (12) of the previous chapter to any dissolved substance which has a vapor pressure, and one given by $p = RTn/V$, and which follows Henry's law. All substances have presumably a certain vapor pressure, however small this may sometimes be. The smaller the vapor pressure, the more accurately does the equation $p = RTn/V$ hold. Equation (12) is repeated below:

$$\bar{F} = RT \ln c + k. \quad (2)$$

It is safe to use Eq. (2), irrespective of the smallness of the vapor pressure, provided the dissolved substance belongs to the class of substances for which Henry's law holds.

We wish to apply Eq. (2) to electrolytes, in order to compute the loss of free energy when a faraday is passed through a cell. Now, the laws of Henry and of Raoult hold or fail together, and we know that Raoult's law does not hold for electrolytes, even in dilute solution, unless we take ionization into account and treat the ions separately as if they were independent molecules. Consequently in applying Eq. (2) to electrolytes, it must not be applied to the electrolyte as a whole, as for example NaCl, but must be applied separately to the ions, as Na^+ and Cl^- .

As applied thus to the ions of electrolytes Eq. (2) is a good approximation when the solution is dilute. The partial molal

free energy of a dissolved electrolyte in any case will be equal to the sum of the partial molal free energies of its ions.

In the cell represented by formula (1) we learned that T_{so_4} equivalents of copper ions and of sulphate ions are transferred per faraday as the joint result of ionic migration and of electrode processes. These are transferred from the concentration c_2 to the concentration c_1 when the current is passed through the cell as written, from left to right. The decrease of free energy of the system caused by such transfer of a gram ion equals the partial molal free energy of the ion in the solution at c_2 minus the partial molal free energy of the ion in the solution at c_1 , or $RT \ln c_2 + k - (RT \ln c_1 + k)$. The decrease of free energy per gram ion of copper transferred is then simply $RT \ln (c_2/c_1)$, and the decrease per gram equivalent is one-half of this, since the valence is two.¹ Since the valence of sulphate ion is also two, the decrease of free energy per gram equivalent of sulphate ion transferred is likewise $\frac{1}{2}RT \ln (c_2/c_1)$. When one faraday is passed, only T_{so_4} gram equivalents of both Cu^{++} and SO_4^{--} are transferred, so that the decrease of free energy per faraday is

$$T_{\text{so}_4}(\frac{1}{2} + \frac{1}{2})RT \ln (c_2/c_1) = T_{\text{so}_4}RT \ln (c_2/c_1). \quad (3)^*$$

This is the whole of the decrease of free energy, for though metallic copper is also transferred from anode to cathode, it is in the same state at either electrode and has the same partial molal free energy.

In the present case there is actually a (positive) decrease, since c_2 exceeds c_1 , making the logarithm positive. We always compute as for a decrease of free energy, and let this turn out positive or negative according to the circumstances.

The electrical work done by the cell is equal to the decrease of free energy attendant upon the changes of state involved in the doing of the work. In physics we learn that the electrical work done by a constant electromotive force E equals the product

¹ The valence may be regarded as the number of gram equivalents per gram ion.

* In case the valences differ, the expression on the right of Eq. (3) must be multiplied by $(\frac{1}{n_1} + \frac{1}{n_2})$, where n_1 , n_2 , are the valences of the respective ions.

of the electromotive force times the quantity of electricity passed (when the current passes in the direction in which E is acting; otherwise, there will be a minus sign). When E is in volts, and the quantity is in coulombs, the work is given in joules (also called volt-coulombs).¹ When one faraday is passed in the direction in which E is acting the work is therefore EF joules, where F stands for 96,510 coulombs.

Equating then the electrical work done per faraday to the loss of free energy per faraday, we have

$$EF = T_{\text{so}_4} RT \ln (c_2/c_1), \quad (4)$$

or

$$E = T_{\text{so}_4} \frac{RT}{F} \ln \left(\frac{c_2}{c_1} \right). \quad (5)$$

Because the electrical work is given in joules, the free energy term in Eqs. (4) and (5) must be similarly expressed. This will be accomplished by expressing R in joules per degree Centigrade absolute and per mole.² The value of R in these suitable units is 8.3123. F is 96,510 coulombs. The value of E consistent with these numbers is given in International volts in terms of the accepted value of the Weston standard cell. This choice of units is of course equally valid for any equation for the electromotive force of a cell.

In calculations, common logarithms (\log) will be used instead of natural logarithms (\ln). Equations such as (5) may be used with common logarithms if we divide the constant ratio R/F by 0.434294, which gives 0.00019832. At 25°, $T = 298.13$, and the factor $RT/(0.434294F)$ becomes 0.059125 for five-figure calculations, or 0.05912 for four-figure calculations, which will usually be more than precise enough. At 18° the factor is 0.05774.

In the case of solutions of copper sulphate, as in most other cases, the transference number varies somewhat with the concentration; thus at 18°, T_{so_4} is 0.673 at 0.5 normal, and 0.625 at 0.05 normal. In deriving Eq. (5) we tacitly assumed that the transference number is independent of the concentration, and

¹ There are ten million ergs in a joule of energy. There are 4.185 joules in a 15° gram-calorie. These factors are for absolute joules. The International joule is larger than the absolute joule, but only by 0.032 per cent.

² The ions are treated as if they were independent molecules,

in using the equation the mean value of the transference number should be taken.¹

We should note that Eq. (5) gives the sign of the electromotive force of the cell correctly. When c_2 exceeds c_1 the logarithm of c_2/c_1 is positive and therefore E is positive, meaning that it tends to drive positive current from left to right through the cell as written, which is of course the case. If c_2 should in another case be less than c_1 , E would be negative, and the equation would show this.

Equation (5) will give the *sign* of the electromotive force of any concentration cell correctly if we write in its cell formula the concentration c_1 on the left and c_2 on the right, as in formula (1), provided the net transfer is from cathodic solution to anodic solution. This provision will be met, if the cations are the ions formed and discharged at the electrodes. But if the anions are the ions formed and discharged at the electrodes, the sign will be reversed.

Equation (5), on the other hand, will not give the magnitude of E correctly for other cells unless the valence of the ions is the same and the number of ions the same which the electrolyte furnishes, as will now appear.

Another example of a cell similar to the copper sulphate cell is that represented by the formula



In this cell there are two so-called hydrogen electrodes, realized by passing hydrogen gas over platinized electrodes at a definite temperature and pressure. Some have supposed that the electromotive force of this cell measures the concentration of hydrogen ions in solution 1, when that in solution 2 is known. When, however, a current is passed from left to right through this cell, T_{cl} moles of H^+ and also of Cl^- are transferred from c_2 to c_1 per faraday, so that the equation for the electromotive force is

$$E = 2T_{cl} \frac{RT}{F} \ln \left(\frac{c_2}{c_1} \right). \quad (7)$$

¹ Strictly speaking, an integration would be necessary, and this is taken into account by specialists. Also we assumed complete ionization, and Eq. (2) for the free energy of the ion, which no present-day specialist would do. Yet he would use an equation very like Eq. (5), except that concentrations are replaced with "activities."

The transfer of hydrogen gas from one electrode to the other is no change of state, but a mere difference of location, and is accompanied by no change of free energy. The electromotive force depends on the change of free energy involved in the transfer of both hydrogen and chloride ions, and we cannot calculate from it the free energy of transfer of hydrogen ions alone, nor the relative hydrogen-ion concentrations. The concentrations c_2 and c_1 are those of hydrochloric acid in the two solutions.

Problems

1. From the information and figures given in the text, calculate the e.m.f., including its sign, of the cell



2. (a) Consider a cell of another type, as follows:



AgCl denotes solid silver chloride. The two KCl solutions are kept saturated with AgCl. No vertical bar is placed between AgCl and KCl, as the electrode process really takes place in the saturated *solution* of AgCl. Transfer of AgCl between solid AgCl and the saturated solution causes no loss of free energy and hence contributes no potential to the e.m.f. The electrode reactions are $\text{Cl}^- + \text{Ag} = \text{AgCl} + \ominus$ and its reverse. The transference number of potassium ion is 0.496 for the stronger and for all weaker solutions of KCl. Consider what happens in the cell when one faraday is passed from left to right and obtain an equation for the e.m.f. of the cell.

(b) Calculate the e.m.f. from your equation and state its sign. The observed numerical value is 38 millivolts.

CHAPTER XVII

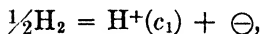
LIQUID JUNCTION POTENTIALS. THE ACTIVITY. THE INFLUENCE OF PRESSURE AND COMPOSITION OF THE ELECTRODE SUBSTANCE

The electromotive forces of many cells are measured, especially by the biologist, for which gain tables as summarized in previous chapters cannot be utilized, or even constructed. The difficulty does not lie in the electrode reactions so often as in the effects of transference. For this reason and also because of the fact that ways of interpreting cells were developed historically before the thermodynamics of cells was commonly understood, we ordinarily distinguish sharply between electrode potentials and liquid junction or "diffusion" potentials, and regard the electromotive force as the algebraic sum of three potential differences, two being located at the electrodes and the other at the junction where the two liquids (if different) meet.

81. Liquid Junction Potentials.—To make this treatment clear, let us discuss again the simple cell



making a slight variation in our manner of summing up the effects, in order to show a principle of great importance in more complicated cases. On passing one faraday through this cell from left to right we have at the anode (left) the reaction



and a reverse reaction at the cathode. The electrode reactions bring about an important transfer of one equivalent of H^+ from HCl of concentration c_2 to HCl (c_1), as well as an unimportant transfer of hydrogen gas from one place to another where it is in the same state.

Assuming the HCl to be completely ionized, the concentration of H^+ will in each case be the same as that of the HCl , and we find

the gain of free energy due to this transfer of H^+ through electrode processes to be $RT \ln c_1 - RT \ln c_2$ or the loss of free energy is $RT \ln (c_2/c_1)$. Hence the electromotive force of the cell would be $(RT/F) \ln (c_2/c_1)$, if the sole change of state were the transfer of hydrogen ions by electrode processes. We may regard this expression as the part of the total electromotive force due to transfer of hydrogen ions by electrode processes.

Through migration of the ions there is transfer of T_H equivalents of H^+ from c_1 to c_2 , and of T_{Cl} equivalents of Cl^- from c_2 to c_1 , which corresponds to a gain of free energy of $T_H RT \ln (c_2/c_1) + T_{Cl} RT \ln (c_1/c_2)$. The corresponding loss of free energy is $-T_H RT \ln (c_2/c_1) + T_{Cl} RT \ln (c_2/c_1)$, or $(T_{Cl} - T_H) RT \ln (c_2/c_1)$. Division of this expression by F gives the electromotive force of a cell in which nothing but this ionic migration occurs, and this electromotive force may be regarded as that part of the total electromotive force of the entire cell that is due to ionic migration. The electromotive force of the entire cell is therefore

$$E = \frac{RT}{F} \ln \left(\frac{c_2}{c_1} \right) + (T_{Cl} - T_H) \frac{RT}{F} \ln \left(\frac{c_2}{c_1} \right). \quad (2)$$

The first term on the right gives the part of the electromotive force due to transfer of hydrogen ion by electrode reaction, and the second term gives the part due to the migration of the ions. We are accustomed to the addition of electromotive forces when they are in series connection, and we naturally imagine that the part due to migration is a difference of potential located at the junction where the two liquids meet, and that the part due to electrode processes is due to the sum of two potentials located at the two electrodes where they meet the liquids.¹

The part of the total electromotive force that corresponds to the loss of free energy due to migration is called the liquid junction, or diffusion, potential. We can account qualitatively for the existence of the liquid junction potential by remembering

¹ Such a sum is naturally an algebraic sum, and may therefore be treated as a difference if we prefer to think of one of the electrode potentials as negative. Let us postpone this matter until the discussion of molal electrode potentials, when a systematic procedure for taking care of the plus and minus signs will be outlined.

that the ions have different mobilities, that for H^+ being greater than for any anion, and that for OH^- being greater than any cation save H^+ . When therefore the concentration c_1 of cell formula (1) is greater than c_2 , there is a tendency of both H^+ and Cl^- ions to diffuse from left to right, and the hydrogen ions, being faster, get ahead a little (though being restrained by the chloride ions, which attract them). This makes the right-hand side of the boundary more positive than the left, and makes the electromotive force of the cell more positive than would be the case were there no migration. But this is also what Eq. (2) shows. For when one ion in a given solution has a greater mobility than a second, its transference number is also the greater.¹ ($T_{Cl} - T_H$) is therefore negative, but so is $\ln (c_2/c_1)$, making the second term on the right-hand side of Eq. (2) positive.

The part of the electromotive force due to the electrode processes receives no special name. It is the electromotive force which a cell would have in which there is no liquid junction potential; it is also the result obtained by subtracting the liquid junction potential from the total electromotive force, or by arranging matters so that the liquid junction potential is eliminated (made practically zero).

When the liquid junction potential is eliminated, either actually or virtually by subtraction of the liquid junction potential from the total electromotive force, two vertical bars instead of one are conventionally written in the formula for the cell at the place where the two liquids, anodic and cathodic, would normally meet. Thus we write



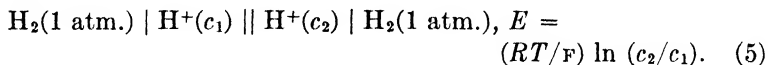
The two bars always mean that the value of E given for the cell is that due solely to the electrode processes, the liquid junction potential having been eliminated, and E corresponds therefore to the loss of free energy of the electrode reactions alone.

We have already found that the electromotive force of this cell (3) is

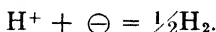
$$E = (RT/F) \ln (c_2/c_1), \quad (4)$$

¹ From Eq. (14), Chap. XIV, $T_{Cl} = U_{Cl}/(U_{Cl} + U_H)$, and $T_H = U_H/(U_{Cl} + U_H)$. Hence, $T_{Cl} - T_H = (U_{Cl} - U_H)/(U_{Cl} + U_H)$. Since the denominator is positive, the numerator has the same sign as the difference of the transference numbers.

since this is the part of the right-hand member of Eq. (2) that refers to the free energy loss due to electrode processes. Furthermore, these electrode processes refer only to the formation or discharge of hydrogen ions, so that we may as well write this cell as follows:



When the liquid junction potential is eliminated, as indicated by the two vertical bars, the electromotive force measures the hydrogen-ion concentration, for if one concentration is known, the other can be calculated from E by the use of Eq. (5). Furthermore, it makes no difference whether the acid is the same in both solutions, or whether it is HCl or some other acid, known or unknown. The solutions may even be alkaline, as they will even then contain hydrogen ions in sufficient amounts to make possible the electrode reaction



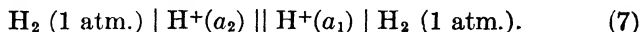
Equation (5) is in fact the foundation for all measurements of hydrogen-ion concentration.

The restrictions on the use of Eq. (5) for the measurement of hydrogen-ion concentration are few, and of an obvious nature. The reactions at the electrodes must be uniquely the electrolytic formation or discharge of hydrogen ions. If one of the solutions contains nitric acid, for example, there will be a chemical reduction of nitric acid by the hydrogen in contact with the platinized electrode, which will make measurements of electromotive force difficult to carry out and impossible to interpret. In general, there will be difficulty when oxidizing substances are present. Another, theoretical, restriction is that the partial molal free energy of hydrogen ion must be given by $RT \ln c + k$. And this is only an approximation. The question, what is the exact expression, by means of which we can calculate the partial molal free energy from the concentration, and therefore also the electromotive force, cannot be completely answered at present, although the theory of Debye and Hückel gives expressions which are satisfactory improvements when the solution is not too strong in electrolytes.

82. The Activity and the Activity Coefficient.—It is very seldom that the biological investigator needs to know the concentration of the ions even when, as in hydrogen-ion work, he is constantly applying equations like Eq. (5). He makes sometimes very precise measurements of electromotive force, and it is embarrassing to refer constantly to the fact that Eq. (5) is only approximate. He rids himself of this embarrassment by substituting the word *activity* for the word *concentration*, and the symbol a for the letter c . Equation (5) becomes simply

$$E = (RT/F) \ln (a_2/a_1) \quad (6)$$

and this equation, now in terms of activities, is exact, as applied to the same cell as before, but which is now written



Here a_2 is the activity of hydrogen ion in a solution whose concentration of HCl is c_2 , and a_1 is the activity of hydrogen ion in the solution whose HCl concentration is c_1 .

How can it be, that an approximate equation is converted into an exact one by such a simple device?

The equality of the decrease of free energy with the electrical work is exact. The equation $\bar{F} = RT \ln c + k$ (Eq. [12] of Chap. XV) is, however, dependent upon the exactness of Henry's or Raoult's law, and is in fact not exact except when the concentration of ions of all sorts is extremely low. We will now define the activity a of the ion to be such as will make the following equation perfectly exact:

$$\bar{F} = RT \ln a + k, \quad (8)$$

where k is the same as in the approximate equation. When the solution is infinitely dilute, the ions are so far apart that they really act as independent molecules, and the partial molal free energy is given by

$$\bar{F} = RT \ln c + k, \quad (9)$$

and the activity a then equals the concentration c , since both equations then hold. When the solution is stronger in electrolytes, Eq. (8) still holds, but not Eq. (9), so that the activity is no longer equal to the concentration.

Hence the equations for the electromotive force become independent of Henry's or Raoult's law, if we merely substitute activities for concentrations in the equations. Through measurements of electromotive force very exact comparisons of activities are possible.¹

In the biological application of hydrogen-ion measurements, we do not really care anything about the *concentration* of the hydrogen ions, as distinguished from their *activity*. The thing we observe is a correlation between electromotive force (or the color effects of indicators) and certain biological or chemical phenomena, and for the purposes of correlation, the electromotive force is better represented by the activity than by the concentration, as it is then unnecessary to refer to Raoult's law in any way.

Even in the case of non-electrolytes, Eq. (9) is not exact in solutions of any considerable strength, whereas Eq. (8) is still exact.

The ratio of the activity of a substance or an ion to its concentration,² a/c , is called the activity coefficient of the substance or ion. It is the number by which the concentration in equations such as Eq. (9) or (5) must be multiplied to make the equation exact.

The activity coefficient of non-electrolytes or of ions approaches the value one as the concentration approaches zero. The activity of a whole electrolyte, such as HCl, does not approach the concentration as the concentration approaches zero, since Raoult's law fails for electrolytes even at infinite dilution, and it is not customary to define its activity coefficient in the same way as for molecules of non-electrolytes or as for ions.³

The idea of the activity is due to G. N. Lewis. Further information on activities and activity coefficients will be found in the work of Lewis and Randall.⁴

¹ The student will not fail to notice that no exact comparisons of *concentrations* are made possible by the substitution.

² In numerical calculations the concentration c used in the activity coefficient is expressed as molality, *i. e.*, in gram moles or gram ions per *kilo* of water.

³ For such a whole electrolyte an activity coefficient is defined with due regard to the number of ions it contains, and to their valences, so that the activity coefficient will still approach unity at infinite dilution (Chap. XX).

⁴ LEWIS and RANDALL, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, Inc., New York, 1923.

83. Cells in Which the Substance of the Electrode Is in Two Different Concentrations or at Two Different Pressures.—The cells considered in Chaps. XVI and XVII are especially simple, in that the electrode substance transferred from one electrode to the other undergoes no change of state, so that the transfer of the electrode substance does not contribute to the electromotive force. Since these cells depend upon a difference of concentration in the two solutions, anodic and cathodic, they are called concentration cells.

There is another type of cell, in which the two solutions have the same concentration, but the electrode substance is in two different concentrations at the two electrodes, or at two different pressures. Thus, we may have a cell in which metallic zinc is used in the form of two solutions in mercury (amalgams). The electrolyte may be zinc sulphate. When current is passed through the cell, zinc ions are formed at the anode and are discharged at the cathode. The mercury does not dissolve appreciably at the anode, as it is too far below zinc in the electromotive series. The mercury serves only to dilute the zinc. The molecular weight of zinc, as for other metals, equals the atomic weight; it dissolves as single atoms in the mercury. Since its valence is two, the equation for the cell turns out to be as follows:

$$\text{Zn}(x_1) \mid \text{ZnSO}_4 (\text{solution}) \mid \text{Zn}(x_2), E = (RT/2F) \ln (x_1/x_2). \quad (10)$$

Amalgams are ordinarily made up by weight, and it is simpler to use mole fractions (x) instead of moles per liter (c), as the density of the amalgam need not be measured. It is also better to use mole fractions in Eq. (10) than concentrations, as Raoult's law is better in terms of mole fractions.

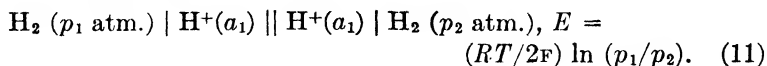
When the electromotive force of a cell of this kind was measured at 30°, the following results were obtained:

Composition	Amalgam 1	Amalgam 2
Percentage of zinc	0.9	0.384
Mole fraction of zinc	0.02711	0.01169

Observed value of E , 10.175 millivolts,¹ value calculated by Eq. (10), 10.982 millivolts.

¹ RICHARDS and GARROD-THOMAS, *Z. physik. Chem.*, **72**, 165 (1910).

An example of this general type of cell, of more importance to the biologist, is the following, in which the electrode substance is hydrogen gas, and occurs at two different pressures:



Instead of using the fact that the solutions about the two electrodes contain dissolved hydrogen at different *concentrations*, we may remember that the partial molal free energy of hydrogen gas at a pressure p is given by the expression $RT \ln p + k$. The electrode reactions are $\frac{1}{2}\text{H}_2 = \text{H}^+ + \ominus$ at the anode, and the reverse at the cathode. When current is passed from left to right, there is transfer of hydrogen gas from p_1 to p_2 at the rate of $\frac{1}{2}$ mole per faraday. This is the reason for the 2 in the coefficient $RT/(2F)$. Since the loss of hydrogen occurs at p_1 , there is a loss of free energy of $\frac{1}{2}RT \ln p_1$, and a minus loss of $\frac{1}{2}RT \ln p_2$, so that Eq. (11) is correct.

One way in which the difference of pressure may be realized is to dilute the hydrogen at one electrode with nitrogen, water vapor, or other inert gas. The total pressure may then be the same at both electrodes. In the expression $RT \ln p + k$, p denotes the partial pressure¹ when the gas is not pure, and the partial pressure may be well enough calculated by multiplying the total pressure by the mole fraction or volume percentage of hydrogen in the mixture.²

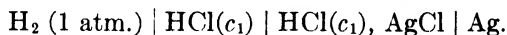
Equation (11) is used for applying corrections to the electromotive force of a cell containing a hydrogen electrode, when we wish the result for 1 atm. and the partial pressure of hydrogen

¹ Better, the *equilibrium pressure* of hydrogen in the mixture (Chap. II). The interested student may note that the partial molal free energy of hydrogen in a mixture must be equal to the free energy of a mole of pure hydrogen at such a pressure that it would be in equilibrium with the hydrogen in the mixture through a semipermeable membrane. But, such a pressure is the equilibrium pressure, or, somewhat ambiguously, the partial pressure.

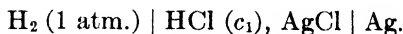
² For high pressures, where this may not be sufficiently exact, we may replace the pressure p in $RT \ln p + k$ with the so-called fugacity, if the relation between the fugacity and the pressure or partial pressure has been determined. The fugacity f is defined by Lewis so as to make the expression $RT \ln f + k$ exactly equal to the free energy of a mole, the k being the same as in the approximate expression, $RT \ln p + k$, for the same gas,

in the cell is not 1 atm., due to variations of the barometer, or to the presence of water vapor in the hydrogen. When the cell contains two hydrogen electrodes, such corrections may ordinarily be omitted, but usually the cell contains only one hydrogen electrode, so that the correction may be necessary. A systematic procedure will be discussed later for combining the electromotive force of several cells in such a way as to obtain the electromotive force of a cell which we need.

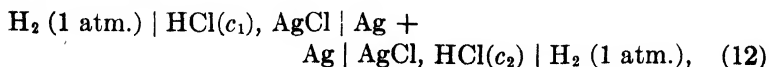
84. Cells without Transference.—These are of interest to the student who looks forward to the study of cells for their theoretical importance, aside from their application to biological problems. When the anode solution of a cell is practically identical in composition with the cathode solution, the migration of the ions produces no change of free energy, and there is no liquid junction potential. Such a cell may be called a *cell without transference* for brevity, instead of the longer and more accurate name, *cell without important effects due to migration*. Consider the cell



Both HCl solutions may be saturated with hydrogen gas at 1 atm., but only the solution on the right ought to be saturated with AgCl. Under these conditions it happens that the hydrogen can reduce silver chloride only through an electrochemical process. The solubility of silver chloride is so low that when the two solutions are of the same strength in hydrochloric acid and hydrogen they may be regarded as practically identical in composition. The cell is usually written accordingly:



When current is passed from left to right, HCl is formed at the concentration c_1 . When therefore current is passed from left to right through the combination



the two silver pieces being connected by a wire, HCl is formed at c_1 and used up at c_2 , in fact, one mole each of H^+ and Cl^- is transferred per faraday from c_2 to c_1 . The electrode processes

in one cell balance those in the other, making the electromotive force of the combination equal to

$$E = (2RT/F) \ln (c_2/c_1). \quad (13)$$

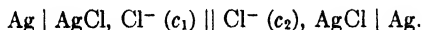
The combination (12) is called the cell without transference corresponding to the cell (1) with transference. When the same two concentrations of HCl are used in each case, the ratio of the values of E gives the transference number of chloride ion (*i. e.*, the average value of T_{Cl} from c_1 to c_2).

Problems

1. Show that Eq. (5) does not hold in general for a cell in which a cation of valence n is transferred from one solution to the other, instead of the univalent hydrogen ion, but that the equation then becomes

$$E = (RT/nF) \ln (c_2/c_1). \quad (14)$$

2. Give reasons why this equation may be used for a cell in which an *anion* is transferred, provided its valence be called negative. An example of such a cell would be



Equations (5) and (14) are usually called the Nernst equation.

CHAPTER XVIII

CHEMICAL CELLS

When we are dealing with concentration cells we are able from general principles to tell the sign of the electromotive force, and even to calculate the value of the electromotive force from the concentrations and the temperature, within the accuracy permitted by the assumption that the ions are "perfect solutes" (*i. e.*, that their partial molal free energy is given by $RT \ln c + k$).

When, however, the operation of the cell involves chemical changes, it requires special knowledge even to predict the sign of the electromotive force. In certain pronounced cases, the sign may be predicted from a sufficient knowledge of ordinary chemistry. In general, however, the electromotive force must be measured directly, or calculated from measurements of chemical equilibria.

85. Single Electrode Potentials and Their Combination.—

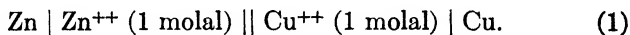
In discussing chemical cells we shall assume in all cases that the liquid junction potential has been eliminated, as indicated in the cell formula by the double vertical bar. The systematic method, which we shall use for combining the electromotive forces of several cells to calculate that of a particular cell, will however enable us to calculate the electromotive force of a cell with liquid junction when the liquid junction potential is known or can be calculated.

A great many electromotive forces have been directly measured, and others calculated from chemical equilibria. The results of this work are largely summarized in the tables of so-called electrode potentials. Subject to the assumption that the ions are perfect solutes, so that their activities are equal to their concentrations, such tables of electrode potentials may be used to calculate the electromotive forces of a great many chemical cells without liquid junction potentials, in a manner now to be explained. Table I gives a brief table of such electrode potentials.

TABLE I.—SOME ELECTRODE POTENTIALS AT 25° IN VOLTS

Half cell	Volts	Half cell	Volts
Pt H ₂ (1 atm.), OH ⁻ (1M)	0.8295	Pt O ₂ (1 atm.), OH ⁻ (1M)	-0.3976
Zn Zn ⁺⁺ (1M)	0.762		
Cd Cd ⁺⁺ (1M)	0.401		
Ag AgI, I ⁻ (1M)	0.151	Pt K ₄ FeCy ₆ (1M),	
H ₂ (1 atm.) H ⁺ (1M).....	0	K ₃ FeCy ₆ (1M),	
Ag AgCl, Cl ⁻ (1M)	-0.222	K ⁺ (1M)	-0.487
Hg Hg ₂ Cl ₂ , Cl ⁻ (1M)	-0.2676	Pt Fe ⁺⁺⁺ (1M),	
Hg Hg ₂ Cl ₂ , KCl (1 N),		Fe ⁺⁺ (1M)	-0.748
KCl (0.1 N) (normal			
calomel electrode).....	-0.2805	Ag Ag ⁺ (1M)	-0.798
0.1 normal calomel elec-			
trode.....	-0.3334	Hg Hg ₂ ⁺⁺ (1M)	-0.799
Cu Cu ⁺⁺ (1M)	-0.344	Au Au ⁺⁺⁺ (1M)	-1.36

Let us explain the meaning and use of this table through a consideration of the cell

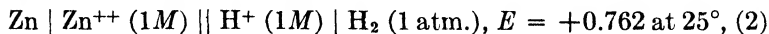


In the operation of this cell only electrode reactions need consideration because of the elimination of the liquid junction potential. The change of free energy per faraday when current is passed through the cell from left to right may be separated in theory into a change due to the anode process ($\frac{1}{2}\text{Zn} = \frac{1}{2}\text{Zn}^{++} + \ominus$), plus a change due to the cathode process ($\frac{1}{2}\text{Cu}^{++} + \ominus = \frac{1}{2}\text{Cu}$). Likewise, the electromotive force of the cell may be separated in theory into a potential difference or simply *potential* at the anode plus a potential at the cathode.

In practice it has not been found possible to determine any such single anode or cathode potential with sufficient precision; hence there is a convention, rather widely adopted, that the single electrode potential of the molal hydrogen electrode shall be considered zero for the purpose of constructing and using a table of single electrode potentials. By the molal hydrogen electrode is meant a hydrogen electrode dipping into a solution in which the activity of the hydrogen ions is 1 molal (*i. e.*, 1

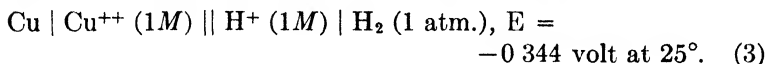
mole per kilo of water, and abbreviated to $1M$)¹ when the solution and electrode are in equilibrium with hydrogen gas at a partial pressure of 1 atm.²

This means that the potential of the zinc electrode, when we write it as $\text{Zn} \mid \text{Zn}^{++} (1M)$ (and not in the opposite manner), equals the electromotive force of the cell

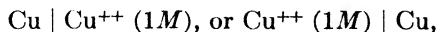


because the potential of the zinc electrode is here written the same as in Table I, where its value is given as +0.762 volt, and the potential of the molal hydrogen electrode is zero, in whichever direction it is written. The positive value of E means there is a tendency of the current to pass through the cell from left to right. Evidently the positive value of the molal zinc electrode similarly means there is a tendency for current to pass through the half cell from left to right, as the half cell is written in the table.

Table I gives the value for the molal copper electrode as -0.344 volt. This means that the electromotive force of the following cell has the value written at the right of its formula



The two molal electrode potentials may be algebraically added or subtracted to obtain the electromotive force of the original cell (1). Whether we should add or subtract depends on the way the molal electrode potential is written; *e. g.*,

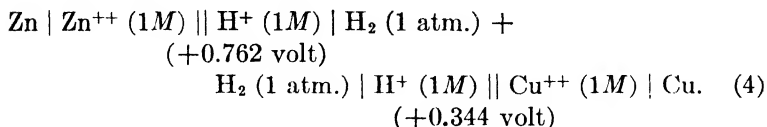


for if the potential is -0.344 volt when written in the former way, it will be +0.344 volt when written in the latter way. Let us consider a procedure for finding out with absolute certainty just how to combine the two potentials.

¹ This is the definition of molality used by Lewis and Randall, whose conventions we are using throughout our discussion of cells.

² Strictly speaking, the so-called fugacity of hydrogen should be equal to 1 atm. This does not ordinarily trouble the biologist, who usually determines in practice his potentials with reference to some calomel electrode.

For this purpose, imagine that we set up the two complete cells (2) and (3) in such a way that the potentials of Zn and of Cu will appear in the same order as in the original cell (1). This will result as follows:



The plus sign between the two cell formulas means that the metals of the hydrogen electrodes are electrically connected by a wire. Now the electromotive force of this combination of two cells is the algebraic sum of the two individual electromotive forces, since the connection is in series, and is therefore +1.106 volts.

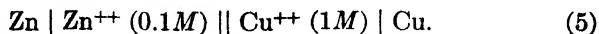
In this combination of cells one hydrogen electrode is written as the opposite of the other, one being used as cathode when the other is used as anode. Any loss of free energy at one hydrogen electrode is therefore balanced by an equal gain at the other, and one hydrogen electrode potential is therefore neutralized by the other, quite apart from the convention that they are both zero in the case of molal hydrogen electrodes.

Therefore these two cells produce in their joint operation the same net change of state and have the same electromotive force as the original cell (1), which has therefore the value $E = +1.106$ volts at 25° .

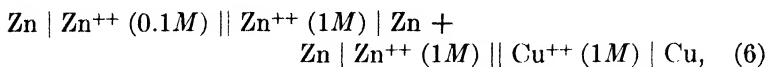
In the same way any two electrodes or half cells, whether molal or not, and whether hydrogen electrodes are involved or not, may be combined to get the electromotive force of a complete cell without liquid junction potential.

The foregoing considerations should make obvious the following rule for finding the electromotive force of any cell without liquid junction potential from tabulated values of the potentials of the two half cells. Add the two potentials, paying attention to signs, after changing the sign of the potential whose half cell appears at the right-hand side of the cell formula in question.

When a cell involves a solution of ions at an activity not molal, the procedure which led to above rule may still be used. As an example, take the cell



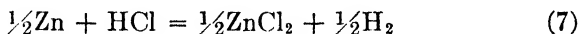
This will have the same electromotive force as the two following cells, connected in series as indicated:



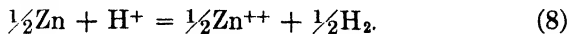
for the two molal zinc electrodes are opposed and their potentials cancel. The first cell is a concentration cell, whose electromotive force will be found to be $(RT/2F) \ln (1/0.1)$ by the application of Eq. (14) of Chap. XVII. The electromotive force of the second cell is found from Table I by the rule just given. The electromotive force of cell (5) is therefore the sum, $(RT/2F) \ln (1/0.1) + 1.106$ volts.

A very extensive list of electrode potentials is given in "International Critical Tables."¹ The methods used in the calculation of such single electrode potentials are described by Lewis and Randall in "Thermodynamics and the Free Energy of Chemical Substances," which may be consulted if it is desired to calculate electromotive forces exactly when concentrations are given rather than activities. For, with the exception of the calomel electrodes, the half cells of Table I specify some ion *activity* as 1 molal.²

86. How to Arrange a Cell for Bringing About a Certain Chemical Reaction.—Suppose we wish to bring about the reaction



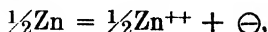
in a voltaic cell. We have only to discover two electrode processes, which will add their effects to produce the above result. This is easier, if we write the equation in the ionic form (canceling out the chloride ions),



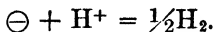
¹ Vol. 6, pp. 332-333.

² When the concentration is given instead of the activity, the first step is to calculate the so-called ionic strength (Lewis and Randall, p. 373, also this book below, Chap. XX). Then from their Table 8, page 382, the activity coefficient of the ion in question may be found. When the concentration is fixed as that of a saturated solution, the problem is a little more complicated, as activity data are then needed for the saturated solution. A typical case is given by them in their discussion of the thallium electrode on page 413, which discussion involves the use of the mass action law.

This immediately suggests the anodic reaction



and the cathodic reaction



We may place some zinc in a conducting solution, for instance, of zinc chloride in a beaker, and some hydrochloric acid together with a hydrogen electrode in another beaker, and connect the two beakers electrically, say with a strip of paper wet with a strong solution of potassium chloride (to reduce the liquid junction potential). If we now connect the zinc with the hydrogen electrode by means of a wire, the reaction (7) will take place as the current flows.

The zinc will probably dissolve faster if we put it in a potassium chloride solution, or some other salt than a zinc salt, but if it is desired to measure the electromotive force, zinc ions must be present around the zinc, so that the reaction $\frac{1}{2}\text{Zn} = \frac{1}{2}\text{Zn}^{++} + \ominus$ can take place in *either* direction as the measurement of electromotive force proceeds. For a definite result, the zinc-ion concentration must be definite. We know that the value of E for the concentration cell $\text{Zn} | \text{Zn}^{++}(c_1) | \text{Zn}^{++}(c) | \text{Zn}$ depends on the value of c , if c_1 is constant. Hence the potential of the half cell $\text{Zn} | \text{Zn}^{++}(c)$ depends on the concentration c . The potential of any half cell depends on the concentrations of the ions or substances taking part in the electrode reaction of the half cell.¹

It will be observed, that to dissolve the zinc electrically with hydrochloric (or indeed any other) acid, we do not place the acid near the zinc, but on the opposite side of the cell. This has been called "chemical action at a distance."

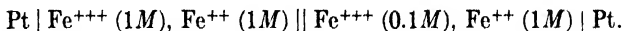
Problems

In these problems, as in the table, the molality refers to the activity. Find the *value* means the sign as well as the numerical value, at 25°.

1. Find the value of E for cell (5).
2. Find the value of E for the cell $\text{Zn} | \text{Zn}^{++} (1M) || \text{Cu}^{++} (0.1M) | \text{Cu}$.

¹ The potential does not depend on other ions or substances, except in so far as these affect the activity coefficients of the ions or substances taking part.

3. Find the value of E for the cell $\text{Hg} | \text{Hg}_2^{++} (1M) || \text{Cd}^{++} (1M) | \text{Cd}$.
4. Find the value of E for the cell



See Eq. (5) of Chap. XIII and consider the changes of state and consequent loss of free energy when current is passed through the cell.

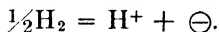
5. (a) Find the electrode reactions by means of which a cell might be arranged for reducing silver chloride with metallic cadmium. (b) Would you have to furnish current, or could you draw current from the cell, in case all the solutions you use are 1 molal?

CHAPTER XIX

CELLS FOR THE DETERMINATION OF HYDROGEN-ION CONCENTRATION OR ACTIVITY

In this chapter the more important cells for the determination of hydrogen-ion activity will be discussed, including certain technical details which involve facts or principles of importance.

87. Hydrogen Electrode Cells.—As mentioned in a previous chapter, the hydrogen electrode can be realized experimentally by passing hydrogen gas through a solution and over the surface of a platinized platinum electrode dipping into the solution. There must be equilibrium with respect to transfer of hydrogen between the gas phase, the solution, and the surface of the platinum; this equilibrium is quickly reached (provided no oxidizing substances are present capable of reacting with hydrogen in the presence of the electrode) if the solution is gently shaken with a limited volume of hydrogen gas in a properly designed electrode vessel, such as that of Clark. There must also be equilibrium with respect to the electrode process



This is easily obtained, as a rule, by the use of an electrode freshly coated with platinum black.

The coating is applied by the electrolysis of a solution of "platinic chloride," making the electrode a cathode. To guard against possible absorption of chlorine by the coating, the coating is then cleansed by cathodic polarization of the electrode in a dilute solution of sulphuric acid, which electrolysis bathes the electrode with hydrogen. The electrode is then well washed with distilled water and not permitted to dry.

Modern technical procedures for the entire experimentation may be found in W. Mansfield Clark's "The Determination of Hydrogen Ions," cited at the end of this chapter.

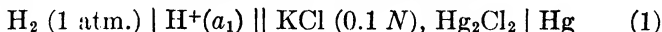
This electronic equilibrium may be obtained by the use of catalytic coatings of other noble metals, such as palladium or iridium, applied to platinum or gold. For most biological fluids,

which are not too acid, palladium is especially convenient, as an old coating may easily be removed by placing the electrode in hydrochloric acid plus a trace of nitric acid, and then replaced with an active, fresh, coating. These metals do not take part in the electrode reaction, and the electromotive force is independent of the catalytic metal.

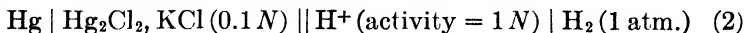
When using cells in purely physicochemical studies, the investigator will probably choose to report his results in terms of the conventions of Lewis and Randall. When using cells for the determination of hydrogen-ion concentration it would seem preferable to follow an authority more interested in the problems of the biologist, such as Clark, for the values of the calomel electrodes and the calculation of pH from electromotive force measurements.¹

With regard to the cell formula and the sign of the electromotive force, the conventions given in previous chapters are strongly recommended in any case. The student should adopt these conventions and adhere to them, even when reading an authority who deviates from them.²

In order to measure the concentration, or better, the *activity* of hydrogen ions in a solution, we set up the cell



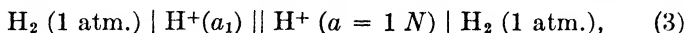
and measure its electromotive force E . The activity of hydrogen ions in the solution is denoted by a_1 . Elimination of the diffusion potential is effected by the use of a salt bridge, as explained below. Now the electromotive force of the cell



¹ See CLARK, "The Determination of Hydrogen Ions," and his article in *International Critical Tables*, Vol. 1, p. 81.

² Anyone having occasion to publish on the e.m.f. of a cell will do well to write his formula for the Daniell cell with its e.m.f., so that an interested reader, who will know the polarity of the Daniell cell, will at once understand the convention used. Thus: $\text{Zn} \mid \text{ZnSO}_4 (\text{satd.}) \parallel \text{CuSO}_4 (\text{satd.}) \mid \text{Cu}$, $E = +1.1$ volts. The plus sign should be added, as some authors unfortunately appear to give the numerical value only, without respect to sign, and without evidence of the use of any particular convention. The same thing can be accomplished in the manner used in parts of "International Critical Tables," by stating the pole sign of one of the electrode metals of each cell in question. The pole sign of the copper in the Daniell cell is positive.

is given at 25° the value -0.3376 volt for the determination of hydrogen-ion concentration or activity, and this is then the value of the decinormal calomel electrode. By considering cell (2) written at the right of cell (1), the two cells being connected in series, we find that the sum of the two electromotive forces, $E - 0.3376$, will be the electromotive force of the single cell



because in the combination the two calomel electrodes are opposed and cancel. But the electromotive force of this cell would be, according to Eq. (6) of Chap. XVII, $(RT/F) \ln (1/a_1)$. Hence,

$$E - 0.3376 = (RT/0.4343F) \log (1/a_1). \quad (4)^1$$

The quantity $\log (1/a)$ is the common logarithm of the reciprocal of the hydrogen-ion activity, and is nothing other than the famous pH of Sørensen. In biological applications it is usual to report this quantity, rather than to take the trouble to solve for the value of a itself. There are a number of reasons why the pH is more convenient to discuss and to plot in diagrams than the activity or concentration itself.

The equation for calculating pH is therefore

$$\text{pH} = \frac{0.4343F}{RT}(E - 0.3376), \quad (5)$$

where E is the electromotive force in volts of the cell (1) at 25°.

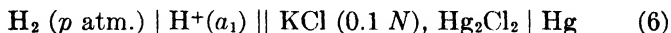
Other reference electrodes than the decinormal electrode may be used, but with a different value of the potential than -0.3376 in Eqs. (4) and (5). Suitable values may be found in Clark's "The Determination of Hydrogen Ions," for various electrodes and various temperatures.²

¹ If we should blindly write cell (1) at the right of cell (2), the result would be $\text{H}^+ (a = 1 N) \mid \text{H}_2 (1 \text{ atm.}) \parallel \text{H}_2 (1 \text{ atm.}) \mid \text{H}^+(a_1)$. This is not the usual way of writing a cell. By reversing both half cells we get formula (3), and as *each* reversal introduces a minus sign, two reversals do not affect the sign.

² CLARK, *ibid.*, Appendix, p. 672. Clark uses an opposite convention for the sign of half cells, so that all his signs may be changed to accord with our convention. The numerical difference between -0.3376 and the value -0.3334 given in Table I of our Chap. XVIII is largely due to difficulties in estimating liquid junction potentials and the activity of hydrogen ion in strongly acid solution.

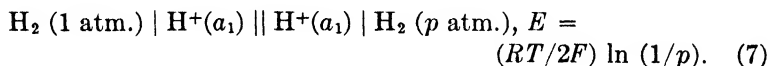
Since the pH is a logarithm, and a logarithm is an exponent, the pH is often called the hydrogen-ion exponent. The value of the pH calculated from Eq. (5) depends on whether -0.3376 , or some other value for the decinormal calomel electrode is used. The "best" value has been the subject of much research. The biological worker should state the value chosen, or the authority followed, when reporting the results of pH studies.

88. The Pressure Correction.—It will not usually be convenient to set up the cell (1) with the partial pressure of hydrogen exactly equal to 1 atm. We shall usually set up the cell



where the partial pressure of hydrogen gas is not exactly 1 atm. but p atm. Let E be the electromotive force of this cell (6). The partial pressure may be obtained by subtracting from the barometric pressure the vapor pressure of pure water at the experimental temperature, or better, the vapor pressure of the solution, when this is known or can be calculated by means of Raoult's law.

In Chap. XVII, Eq. (11), we found an equation for the electromotive force of a cell with the hydrogen at two different pressures. Putting $p_1 = 1$, and $p_2 = p$, we have the cell



The electromotive force of the two cells (6) and (7) in series will be

$$E + \frac{RT}{2F} \ln \left(\frac{1}{p} \right).$$

When the two formulas are written in sequence, (6) to the right of (7), it will be seen that the two electrodes with hydrogen at p atm. are opposed, so that the two cells are equivalent to the single cell (1), the electromotive force of which is therefore

$$E - \frac{RT}{0.4343 \times 2F} \log p.$$

This expression may therefore be used in Eq. (5) to find the pH, giving the result

$$\text{pH} = \frac{0.4343F}{RT} \left(E - \frac{RT}{0.4343 \times 2F} \log p - 0.3376 \right). \quad (8)$$

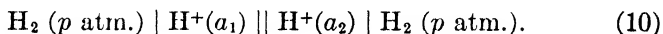
This can be simplified to the following:

$$\text{pH} = \frac{0.4343F}{RT} (E - 0.3376) - \frac{1}{2} \log p, \quad (9)$$

where, as in Eq. (8), E is the electromotive force of cell (6).

The pressure correction, $-\frac{1}{2} \log p$, is independent of the calomel or other reference electrode. In it, p must be expressed in atmospheres. For many purposes the pressure correction is small enough to be disregarded.

To avoid the necessity of a pressure correction, some investigators prefer to set up the cell



The total pressure will be made the same on both electrodes, and the partial pressures will then be very nearly the same (since the temperature is of course the same) unless the two solutions differ greatly in vapor pressure. The student should verify the following, where E is the electromotive force of cell (10):

$$E_F = RT \ln \left(\frac{a_2}{a_1} \right) = \frac{RT}{0.4343} (\log a_2 - \log a_1) = \frac{RT}{0.4343} (\text{pH}_1 - \text{pH}_2). \quad (11)$$

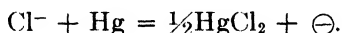
Hence,
$$\text{pH}_1 = \text{pH}_2 + \frac{0.4343F}{RT} E. \quad (12)$$

Equation (12) may be used to calculate pH_1 when the pH of another solution, pH_2 , is known and E is measured for the cell (10). The electromotive force of cell (10) will be positive (and the pole sign of the platinum on the right, positive) when pH_1 is greater than pH_2 . Then the activity of hydrogen ions on the left (a_1) will be less than that on the right (a_2), and the

solution on the left will be in general less intensely acid, or more intensely alkaline. This is because the pH is the logarithm of the *reciprocal* of the hydrogen-ion activity, and is therefore greater in alkaline solution than in acid solution.

In the case of cells (1) and (6), the electromotive force will be positive when (a_1) corresponds to an alkaline solution, and the pole sign of the mercury will be positive. If the alkalinity be made to decrease, and the acidity therefore to increase, the electromotive force will decrease, and may reach zero and finally change sign. The pH at which the sign changes depends of course on the potential of the particular reference electrode which may be used instead of the decinormal calomel electrode.

89. Calomel Electrodes.—The calomel electrodes used in pH studies are ordinarily potassium chloride calomel electrodes. The *decinormal*, or other prefixed description, refers to the strength of the potassium chloride. Essentially, the electrode consists of a solution of potassium chloride saturated with calomel (Hg_2Cl_2) in contact with mercury. Electrical connection with the mercury is made by means of a wire dipping into it, but insulated from the solution. An excess of finely divided calomel is necessary.¹ The electrode reaction is



The solution is to be kept saturated with calomel. The change of free energy attending the electrode reaction will depend on the activity of the chloride ion, and therefore on its concentration. The potential of the calomel electrode depends therefore on the concentration of potassium chloride, as well as on the temperature. In the saturated calomel electrode, a saturated solution of potassium chloride is used. This electrode has especial convenience in practice, but the student will note that constancy of potential will depend (aside from constancy of temperature) upon keeping the solution saturated, not only with calomel, but also with potassium chloride. Its potential is -0.2458 volt at 25° .

¹ Measurements of e. m. f. are capable of such a high degree of precision that it makes some difference just how finely divided the calomel is. Experimental details should be sought in technical books.

90. The Salt Bridge.—In the measurement of electromotive force for pH determination, the elimination of the liquid junction is believed to be accomplished in most cases within about one millivolt by means of the so-called salt bridge. This consists of a saturated solution of potassium chloride, which is brought into contact with the solution of hydrogen ion on one side and with the calomel or other reference electrode on the other. The liquid junction potential between saturated potassium chloride and decinormal potassium chloride solutions is small and is included in the value of the decinormal electrode given for pH work, so that it is correct to ignore it. The liquid junction potential of saturated potassium chloride solution against the solution of hydrogen ion depends on many factors, but it is probably sufficiently small when the solution is neither very acid nor very alkaline.

The technique of producing the junction has been improved in recent years, and the "flowing junction" has been developed. An apparatus is necessary which will permit the two solutions to flow continuously into a tube in which they are stratified. This technique makes it possible to obtain very precisely reproducible results; it does not necessarily eliminate the potential more completely.

91. The Potentiometer.—Only a few of the half cells discussed above, and listed in tables of electrode potentials, can be combined to form practical cells, capable of delivering current enough to run electrical appliances. Indeed, many of the combinations, as they will ordinarily be made, will not be able to "run" an ordinary voltmeter, so that the voltage measured on such a voltmeter will be much less than the electromotive force (which is the terminal voltage when no current is being drawn), and perhaps insufficient to give a deflection of the pointer.

The potentiometer is a device which measures the voltage when no current is being drawn. In order to make the necessary adjustment, only the small current necessary to swing the pointer of a very sensitive galvanometer one way or the other needs to be drawn from the cell. The instrument is brought into such an adjustment that no movement of the galvanometer pointer will be produced when the circuit is momentarily completed by depressing a key.

Figure 35 shows the essentials of a potentiometer without some of the conveniences which are attached to a commercial instrument. AD represents a fixed resistance with moving contacts B and C . (In commercial instruments AD will be a combination of coils in series, with or without a slide wire also in series.) A constant current from a two-volt lead storage cell is passed through AD and through a regulating resistance R . The value of the current can be made correct by connecting a standard cell of known electromotive force to the potentiometer and varying R until the instrument measures it correctly. In commercial instruments special contacts, as A and E , are usually provided, as well as a special switch, to put either the standard cell, or the unknown cell, into its proper connection. G is a sensitive galvanometer,¹ usually sold as a separate instrument, and K a key on the potentiometer. When the current through BC is constant the voltage e between the points B and C is proportional to the resistance r from B to C according to Ohm's law: $I = e/r$. A commercial instrument will be calibrated to give on the dials the voltage drop along CB , which is possible since the current I is always the same through BC when taking readings.

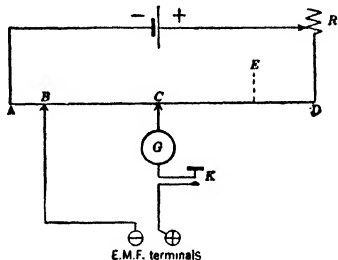


Fig. 35.—Wiring diagram of a potentiometer.

We attach wires from a cell of unknown electromotive force to the plus and minus e.m.f. terminals of the potentiometer, set the contacts B and C to some reasonable value, and tap the key closed for as short a time as possible (to avoid too great a swing of the galvanometer pointer), observing which way the pointer swings. We now change the contacts B and C and test and finally arrive at an adjustment such that the pointer does not move when we depress the key even for a second or two (the time for the coil of the galvanometer to get into motion). We now check the current through the potentiometer, by the use

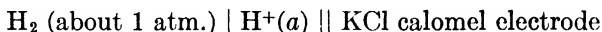
¹ For pH work, the resistance of the sensitive galvanometer should be fairly high, say about 400 ohms, to match the fairly high resistance of the cells used.

of the standard cell, and repeat the adjustment if necessary.¹ The reading of the dials of the potentiometer is now the electromotive force of the cell in question, for when the pointer does not move, no current is passing through the branch of the circuit containing the cell, the current I through the potentiometer is correct, and the only condition that can account for failure of the pointer to move is equality of the electromotive force of the cell with the voltage drop along CB , which voltage drop is graduated on the dials.

Now, this adjustment cannot be obtained unless the unknown cell is connected properly to the e.m.f. terminals of the potentiometer, plus to plus, and minus to minus, so that the two voltages are in opposition. If, therefore, we find that we cannot obtain an adjustment, we shall suspect that the cell is improperly connected and shall therefore reverse the connections. Of course we cannot get a balance if the electromotive force of the cell lies outside the range of the instrument, but this is improbable unless the potentiometer has two ranges and we select the wrong one.

When we know nothing about the polarity of an unknown cell we can determine it by observing which of its electrodes must be connected to the plus e.m.f. terminal of the potentiometer in order to obtain a balance. Then if the cell formula is written with this electrode on the right, the electromotive force of the cell as thus written will be positive.

When using any standard calomel electrode the electromotive force of the cell



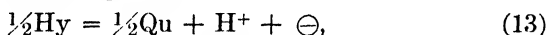
will be positive when $\text{H}^+(a)$ refers to any fluid met in biological work. We may therefore secure the correct connection to the potentiometer by connecting the wire from the calomel electrode to the plus e.m.f. terminal of the potentiometer. Any experimenter will find it convenient to arrange his cells on the desk in the same order as he has written, or proposes to write, the cell formula. This will be of special help when he is dealing with

¹ It is convenient to keep the storage cell delivering (about) the right current through the potentiometer continually (day and night) when e.m.f. measurements are being made, as the voltage of the storage cell stays quite constant in that case for days.

oxidation-reduction cells, as the polarity of these is likely to be changed during a series of measurements.

92. The Quinhydrone Electrode.—For the measurement of pH, other electrodes than the hydrogen electrode may be used. We shall here consider the quinhydrone electrode of Biilmann because of its convenience and wide use.

Hydroquinone, with a formula we shall represent by Hy, is used in photography. It can be oxidized to quinone (Qu) when it is present at the anode of a cell in which current is passing, according to the electrode process



and, similarly, quinone can be reduced if present at a cathode, according to the reverse process, hydrogen ion being furnished by water, if necessary. Since this electrode process involves the production or removal of hydrogen ions, the electromotive force of a cell made up of such an electrode plus another such or a standard reference electrode, with elimination of liquid junction potential, depends on the hydrogen-ion activity and can be used to measure it.

For this purpose we must have hydroquinone and quinone present in the solution whose hydrogen-ion activity is to be determined. The electromotive force will depend on their concentrations, as well as on the hydrogen-ion concentration. It is therefore in some respects convenient, that hydroquinone and quinone form a compound, called quinhydrone, which contains one mole of each, and has a small but sufficient solubility in water. When dissolved in water, it can readily dissociate into its two components, either of which can be converted into the other by oxidation or reduction.

To determine the pH of a solution 1 we may set up a quinhydrone electrode by adding to the solution solid quinhydrone (QH), and shaking to form a saturated solution. A convenient way is now to make a similar quinhydrone electrode, using a solution 2 of known pH.¹ Connect the two solutions with a salt bridge in the order given below:



¹ Directions are given in Clark's "The Determination of Hydrogen Ions," and in other technical books for making up solutions of almost any desired pH value. They are usually called buffer solutions.

A piece of noble metal, such as platinum or gold, which need not be coated with platinum or other black, is immersed in each solution. This metal does not enter the electrode process and serves only to supply electrons to the solution or to extract them. On passing current from left to right through the cell, electrons enter the cathodic solution on the right and H^+ ions are discharged and reduce quinone, while the opposite occurs at the anode on the left. Per faraday, one equivalent of hydrogen ion is removed from solution 2 and added to solution 1. In other respects the effects at one electrode are balanced by those at the other. The electromotive force of the cell (14) is therefore given by

$$E_F = RT \ln \left(\frac{a_2}{a_1} \right) = \frac{RT}{0.4343} (\log a_2 - \log a_1) = \frac{RT}{0.4343} (pH_1 - pH_2). \quad (15)$$

From this may readily be found, that

$$pH_1 = pH_2 + \frac{0.4343F}{RT} E, \quad (16)$$

where E is the electromotive force of cell (14). This equation is the same as Eq. (12), and for obvious reasons.

If preferred, some calomel electrode may be used as a reference electrode.

93. Refinement of the Quinhydrone Electrode.—We have assumed above that, because the solution of hydrogen ion to be studied is saturated with quinhydrone, the change of free energy due to the substitution of hydroquinone for quinone is the same in different solutions and hence that the electromotive force of cell (14) is determined solely by the two activities a_1 and a_2 of hydrogen ion. Now the free energy change due to the substitution will be the same if the partial molal free energies of both quinone and hydroquinone are the same in all solutions. This is approximately the case when all solutions are saturated with quinhydrone. But, strictly speaking, all that is guaranteed by saturating the solutions with quinhydrone is that the partial molal free energy of quinhydrone is the same in all solutions, or

that the sum of the partial molal free energies of hydroquinone and quinone in all solutions is constant.¹

The change of free energy due to the substitution may be made exactly the same in all solutions at the same temperature by saturating them with both quinhydrone and hydroquinone, or with both quinhydrone and quinone. Electrodes so prepared are called hydro-quinhydrone and quino-quinhydrone electrodes, respectively.

For many purposes it will be sufficient to saturate with quinhydrone alone. Indeed, in so far as we may trust the approximate expression $RT \ln c + k$ for the partial molal free energy of a dissolved substance, there will be no difficulty.²

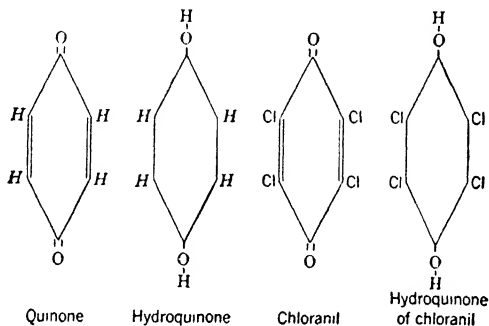


FIG. 36.

The chloranil electrode is coming into use. The solutions are saturated with both chloranil and its hydroquinone (Fig. 36). (The hydrogen atoms represented in slant letters are understood by the organic chemist without writing them.) These two substances do not form an insoluble compound like quinhydrone.

¹ Since dissolved quinhydrone is in equilibrium with hydroquinone and quinone, according to the equation



the partial molal free energy of quinhydrone must be equal to the sum of the partial molal free energies of the hydroquinone and quinone, in order that the change of free energy should be zero when the reaction is conducted at constant temperature and pressure (see Chap. XV).

² The quinhydrone electrode gives exact results when the ratio of the activity coefficients of the hydroquinone and quinone in solution remains constant in all the solutions.

94. Limitations to the Use of Hydrogen or Quinhydrone Electrodes.—We cannot in general secure a constant, reproducible, and interpretable electromotive force if the cell permits more than one chemical process, and that one an electrode reaction, at either electrode.¹ For this reason the hydrogen electrode cannot generally be used when the solution to be tested contains easily reducible substances, because the catalytic coating of platinum or other black often brings about a chemical reduction by hydrogen gas. In the case of the quinhydrone electrode no coating is necessary, and even such solutions as dilute nitric acid have been measured. In this case, nitric acid "ought" to oxidize the hydroquinone, but fails to do so fast enough to interfere. Success can hardly be predicted in such cases.

Similarly, in the case of the hydrogen electrode, air must be kept from leaking into the electrode vessel during the measurement, as oxygen combines with hydrogen in the presence of a catalytic coating, thus greatly reducing the partial pressure of hydrogen in the immediate vicinity of the electrode metal and giving altogether false results.² The supply of hydrogen ought to be free from oxygen, but if a limited volume of reasonably pure hydrogen is shaken with the platinum electrode as in the Clark electrode vessel, the oxygen is used up, and a correct electromotive force can be obtained.

The quinhydrone electrode is much less affected by oxygen, and usually no special precautions are taken to exclude air, other than complete immersion of the metallic electrode.

Certain feebly acid solutions containing dissolved carbon dioxide (or alkaline solutions containing ammonia) may change in pH if, in the measurement with the hydrogen electrode, too much dissolved gas is driven out by a stream of hydrogen or evaporates into the hydrogen atmosphere. Such solutions may be measured, by using the same limited volume of hydrogen repeatedly with

¹ We do not of course intend here to exclude a chemical process which always attains equilibrium and is taken account of in the formula for the electrode reaction.

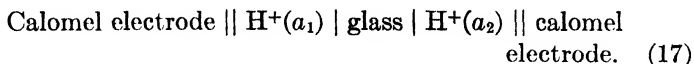
² The oxygen may also enter directly into an electrode reaction. Unfortunately, this electrode reaction, $\frac{1}{2}\text{H}_2\text{O} + \frac{1}{4}\text{O}_2 + \ominus = \text{OH}^-$, cannot apparently be realized without undesirable secondary reactions, or a useful method of determining pH might be based upon it.

fresh portions of the solution to be tested. In this way the partial pressure of gas in the hydrogen mixture can be brought to such a value that it is practically in equilibrium with unchanged solution. In precise work, the partial pressure of hydrogen in this gas mixture should be determined, and a correction applied [Eq. (9)]. For such solutions the quinhydrone electrode is more convenient, when it may be used.

Hydroquinone is itself a weak acid, capable of combining with base in alkaline solution. It may not therefore be added to an alkaline solution of unknown pH to determine this pH, as the addition will make the solution to be tested less alkaline than it was originally. A practical limit would be about pH = 8. But in alkaline solution the hydroquinone is furthermore too readily oxidized by various substances, so that the practical limit is more nearly pH = 6 or 7, depending on circumstances, and on the precision desired.

Certain substances may "poison" an electrode, especially a hydrogen electrode. They may hinder the electrode process desired, take part in an undesired electrode process, or chemically react with electrode substances. Some solutions of arsenic compounds evidently coat the platinum with arsenic, permanently destroying its necessary catalytic properties. Careful workers never permit a coated platinum electrode to become dry, and they frequently remove the old coating and put on a new one.

95. The Glass Electrode.—A remarkable cell for the measurement of pH is the following:



Two salt bridges are used. The glass is a glass membrane and very thin, not more than about 0.025 mm. thick.¹ Such membranes were first extensively studied by Haber and Klemenziewicz. Even with the thinnest membranes, an ordinary high sensitivity galvanometer will not receive enough current through the glass membrane to operate satisfactorily, and a quadrant

¹ MacInnes and Dole have recently described a simple method of producing glass electrodes with membranes only about 0.001 mm. thick. *Industrial and Eng. Chem., Analyt. Ed.*, **1**, 57 (Apr. 15, 1929). See also their paper in *J. Am. Chem. Soc.*, **52**, 29 (1930).

electrometer is generally used, which takes only enough current to charge its plates. Owing to the very high resistance of the cell, the insulation must be extraordinarily effective so that the electrometer does not receive any charge from a source other than the cell. Recently a new vacuum tube has been successfully used to replace the quadrant electrometer.¹

Not all glasses are equally suitable.² If the glass has a suitable composition and is in contact with solutions not too alkaline, it seems to act at both surfaces as an electrode reversible to hydrogen ions alone, that is to say, hydrogen ions are somehow absorbed at one surface and delivered at the other when current is passed without the occurrence of other important changes of state. The two calomel electrodes are alike, are opposed, and do not contribute to the electromotive force, which is therefore

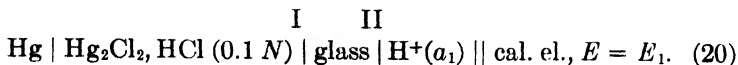
$$E = (RT/r) \ln (a_1/a_2). \quad (18)$$

Hence,

$$\text{pH}_2 = \text{pH}_1 + \frac{0.4343F}{RT} E. \quad (19)$$

When pH_1 is known, pH_2 may therefore be found from the electromotive force E of cell (17) by means of Eq. (19).

The glass membrane may not have quite the same properties at the two surfaces, so that the electromotive force may be changed in magnitude, as well as in sign, if the two solutions are interchanged. It is better therefore to use the principle of substitution. One salt bridge may be omitted, and a cell set up such as

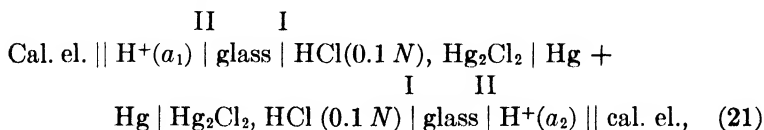


The electrode at the left is a hydrogen chloride calomel electrode, not necessarily of the concentration indicated. The calomel electrode at the right is an ordinary potassium chloride calomel electrode. The glass surfaces are distinguished as I and II. Let the electromotive force be E_1 when a solution of known pH_1

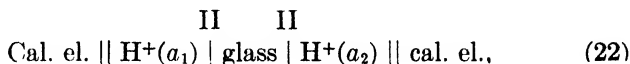
¹ HILL, S. E., *Science*, **73**, 529 (May 15, 1931). The tube is the General Electric Plotron FP 54. Any tube can be used if its grid is biased at floating-grid potential.

² See papers of MacInnes and Dole cited on page 169.

and activity a_1 is used as shown, and let the electromotive force be E_2 when the solution of activity a_1 is replaced with another of activity a_2 and pH_2 . Then by taking the difference, $E_2 - E_1$, all the calomel electrodes, as well as the surface I of the glass next to the HCl solution, are eliminated. $E_2 - E_1$ will be the electromotive force of the combination of two cells in series:



and the changes of state on passing current will be the same as in the cell



whose electromotive force is

$$\frac{RT}{0.4343F} \log \left(\frac{a_1}{a_2} \right) = \frac{RT}{0.4343F} (\text{pH}_2 - \text{pH}_1) = E_2 - E_1. \quad (23)$$

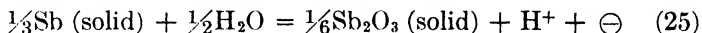
$$\text{Hence,} \quad \text{pH}_2 = \text{pH}_1 + \frac{0.4343F}{RT} (E_2 - E_1). \quad (24)$$

The electromotive force of cell (20) as written will be positive, so long as pH_1 or pH_2 is greater than about 2, as will be the case for most biological fluids. It makes a difference what KCl calomel electrode is used, but the previous statement holds good even in the worst case, in which the saturated potassium chloride calomel electrode is used.

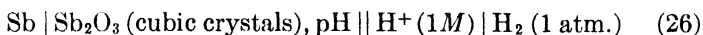
The glass electrode is especially useful for the measurement of pH of strongly oxidizing solutions, or for measuring the pH of very small quantities of fluid. It has been applied even to solutions of permanganate. If, however, the solution is too alkaline, the glass electrode fails, apparently because the glass takes on the character of a K^+ or Na^+ electrode, rather than that of a H^+ electrode.

96. The Antimony Electrode.—Metallic antimony can undergo oxidation at an anode with the production of hydrogen ion and of an oxide, Sb_2O_3 , of low solubility. An antimony electrode,

consisting of antimony in intimate contact with the trioxide and immersed in a solution of a definite pH, can be used to measure this pH. The electrochemical reaction



can be realized under suitable conditions. The electromotive force of the cell



was found by Roberts and Fenwick¹ to be

$$E = -0.1445 + 0.05915 \text{ pH, at } 25^\circ, \quad (27)$$

where pH is that of the solution in which the antimony and its cubic trioxide are immersed. They were able to verify this equation by (1) using cubic Sb_2O_3 , carefully avoiding the presence of any unstable solid phase, notably orthorhombic trioxide, (2) eliminating dissolved oxygen from the system, and (3) approaching the equilibrium from the alkaline side. Under these conditions the electromotive force E is a linear function of pH, with the theoretical slope 0.05915, from pH 1 to 10, and within 0.06 millivolt.

The electrode has been applied without these precautions by a number of biological investigators, who have usually found the slope to be less than the theoretical, and to vary with the pH. When the electrode is so applied, it should certainly be checked, in the region of pH where it is to be used, by means of solutions of known pH.

Book References

Some books of especial importance in connection with the measurement of hydrogen-ion concentration are Clark: *The Determination of Hydrogen Ions*, 3d ed., The Williams and Wilkins Company, Baltimore, 1928; Michaelis: *Hydrogen Ion Concentration*, translated by Perlzweig, The Williams and Wilkins Company, Baltimore, 1926; and, for all sorts of technical information relating to physical chemistry, Ostwald-Luther, *Hand- und Hilfsbuch zur Ausführung physiko-chemischer Messungen*. 15th ed., Akademische Verlagsgesellschaft, M. B. H., Leipzig, 1931.

¹ *J. Am. Chem. Soc.*, **50**, 2125 (1928).

Problems

1. (a) From the definition of pH, show that when the hydrogen-ion activity is 2×10^{-5} , the pH value is 4.70. (b) Find the pH corresponding to the activity 4.6×10^{-7} . (c) Find the activity corresponding to $\text{pH} = 9.8$.

2. The value of E for the cell $\text{H}_2 (1 \text{ atm.}) \mid \text{H}^+(a_1) \parallel \text{KCl} (0.1 N), \text{Hg}_2\text{Cl}_2 \mid \text{Hg}$ is found to be 0.610 volt at 25° . What is the pH corresponding to a_1 ?

3. If the activity of hydrogen ions in the cell of Prob. 2 is made great enough, the e.m.f. might change sign. (a) Show that this point would be reached at about $\text{pH} = -5.7$. (b) The potential of the saturated KCl calomel electrode is -0.2458 volt at 25° . Show that if this electrode is used in the cell of Prob. 2 instead of the decinormal electrode the sign would change at about $\text{pH} = -4.2$.

Since the pH of fluids of biological origin does not become negative, it is evident that the value of E will not change sign in ordinary biological work, when potassium chloride calomel electrodes are used for determining pH.

CHAPTER XX

THE LAW OF MASS ACTION

It is hardly possible to develop the applications of pH measurements without frequent reference to the law of mass action, nor to discuss adequately the use of indicators for the determination of pH. This law enters into all cases of chemical equilibrium, and there are but few chemical reactions which come to our attention without suggesting the idea of chemical equilibrium.

97. Mass Action Law and Mass Action Constant.—We usually think of the neutralization of a base by an acid as being a quantitative reaction, proceeding to completion according to a chemical equation. Yet, if either base or acid (or both) be weak, the neutralization is in fact incomplete when chemical equivalents of base and acid are mixed, and when the mixture comes to equilibrium we have certain concentrations of base and of acid existing in equilibrium with the salt and water produced in the reaction. In such a case, it is also found that the salt in question, if purified and then dissolved in water, is partly decomposed again into base and acid, that is, is hydrolyzed. We meet so many cases of equilibrium of this sort that we have come to regard the incomplete or balanced reaction as the normal thing to expect; and when a chemical reaction seems to be quantitative, we generally say that the equilibrium lies far on one side, assuming herewith that by methods sufficiently delicate we should be able to show the presence of some unchanged substance. We furthermore generally suppose that the reaction may be made to proceed in the reverse direction by properly regulating the concentrations, since it is common experience that a chemical reaction may go one way, or the opposite, according to the concentrations of the substances involved.

The mass action law is a mathematical relation which these concentrations must satisfy when equilibrium with respect to the chemical reaction is reached. An appreciation of the form

of the law is often helpful, and when we also know a number which enters the mathematical relation—the mass action constant—we can usually arrange matters in such a way as to make possible a calculation of the yield of the process.

The mass action law results from the proposition announced in Chap. XX that if a system is in chemical equilibrium, the change of free energy will be zero when a change of state is supposed to take place at constant temperature and pressure. This change of state will be specified by means of the chemical equation for the reaction, plus a statement of the temperature and pressure and information when necessary as to the state of aggregation of the substances involved. In order to derive the mass action law from this proposition, all we need to know is the relation between the partial molal free energy of each substance and the concentration or partial pressure, and we have for this the approximations (Chap. XX): $RT \ln p + I$ for a gas, when p is the partial pressure of the gas; $RT \ln c_1 + k_1$ for a dissolved substance at concentration c_1 in dilute solution; and $RT \ln x_0 + k_0$ for the solvent in a dilute solution, where x_0 is the mole fraction of the solvent.

The constants I , k_1 , k_0 , etc., are usually unknown. In our discussion of concentration cells they were eliminated by subtraction. In the present discussion they will be collected and combined to form a single constant, that usually has to be determined by special experiment.

Let us consider a definite chemical reaction, the decomposition of hydrogen iodide according to the equation



At an elevated temperature, say about 450° , all the substances are gases, and the reaction is a balanced one, coming soon to equilibrium. Consider a mixture of these gases in any proportions consistent with equilibrium, not necessarily equal moles of H_2 and I_2 . If, starting with equilibrium, the reaction is supposed to go a little further from left to right at constant temperature and pressure, the corresponding change of free energy must be zero. For every mole of iodine formed, the gain of free energy would be equal to the partial molal free energy of hydrogen \bar{F}_{H} , plus that of a mole of iodine \bar{F}_{I} , minus twice

that of hydrogen iodide, $2\bar{F}_{\text{HI}}$; and this algebraic sum must come out zero, that is, $\bar{F}_{\text{H}} + \bar{F}_{\text{I}} - 2\bar{F}_{\text{HI}} = 0$. This can be rearranged to conform with Eq. (1), as follows:

$$2\bar{F}_{\text{HI}} = \bar{F}_{\text{H}} + \bar{F}_{\text{I}}. \quad (2)$$

Equation (2) is the same as the chemical equation (1), except that the symbols for the chemical molecules have been replaced by symbols for the partial molal free energy of the corresponding substance. Gibbs taught us, that whenever there is equilibrium with respect to a chemical reaction, the chemical equation for the reaction applies in terms of the partial molal free energies, as well as in terms of the molecule and mole. This is the most simple and elegant, and an exact, statement of the law of mass action.

A useful approximate mass expression may be obtained by substituting into Eq. (2) expressions of the form $RT \ln (px) + I$ for the partial molal free energy of each gas. In this expression p is the pressure of the gas mixture, and x the mole fraction of the particular gas in the mixture, so that px is the "partial pressure" of the gas (see Prob. 3, Chap. XV). Making the substitution for each gas, and using subscripts to identify the mole fractions and constants, we have

$$RT \ln px_{\text{H}_2} + I_{\text{H}_2} + RT \ln px_{\text{I}_2} + I_{\text{I}_2} - 2RT \ln px_{\text{HI}} - 2I_{\text{HI}} = 0. \quad (3)$$

For our later convenience, we have here also changed the sign of each term. We may rearrange this equation as follows:

$$RT[\ln px_{\text{H}_2} + \ln px_{\text{I}_2} - \ln (px_{\text{HI}})^2] = 2I_{\text{HI}} - I_{\text{H}_2} - I_{\text{I}_2}, \quad (4)$$

or, rearranging again,

$$\ln \frac{(px_{\text{H}_2})(px_{\text{I}_2})}{(px_{\text{HI}})^2} = \frac{2I_{\text{HI}} - I_{\text{H}_2} - I_{\text{I}_2}}{RT}. \quad (5)$$

Since all the I constants are fixed by the temperature, the whole expression on the right of Eq. (5) is constant at constant temperature, and it may be regarded as the natural logarithm of another constant K_p , which is called the mass action constant in terms of partial pressures for the reaction (1). Hence,

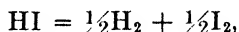
$$\frac{(px_{\text{H}_2}) \times (px_{\text{I}_2})}{(px_{\text{HI}})^2} = K_p. \quad (6)$$

We use the qualifying phrase *in terms of partial pressures*, because the outline or function

$$\frac{()_{\text{H}_2} \times ()_{\text{I}_2}}{()_{\text{HI}}^2},$$

is sometimes filled in by inserting into the parentheses other quantities than the partial pressures; for instance, concentrations in moles per liter, the mole fractions alone, or activities, etc. For brevity we may distinguish the expression in Eq. (6) as the mass action function of the partial pressures.

The reason for changing the sign of each term in obtaining first Eq. (3) and finally Eq. (6) was, that we wish the products of the reaction (1) to be represented in the numerator of the fraction of Eq. (6), and the reactant (HI) to appear in the denominator. It is a convention almost universally followed, to write the chemical reaction, and then write the mass action expression to correspond, placing the *products* of the reaction, as written, in the *numerator* of the mass action function, and the *reactants* in the *denominator*. In this way, the larger the value of the constant, the more complete the reaction from left to right. We shall always follow this convention. The reaction itself may however be written as in Eq. (1) above, or with fractional moles, as



in which case the mass action constant will be written to correspond.

It must be observed that the partial pressure of HI in Eq. (6) is raised to the second power. This is because two moles of HI are written in Eq. (1). In writing any mass action function, exponents are placed over the parentheses, which exponents are equal to the coefficients in the chemical equation. Thus, the outline for the reaction



is

$$\frac{()^{\frac{1}{2}}_{\text{H}_2} \times ()^{\frac{1}{2}}_{\text{I}_2}}{()_{\text{HI}}}.$$

It happens in the decomposition of hydrogen iodide that the number of moles formed by the reaction equals the number of

moles that disappear. In such a special case, a number of simplifications are possible which are not generally possible. Thus, the pressures may be wholly eliminated by cancellation from the mass action expression (6), leaving the mass action function of the mole fractions equal to a constant. In such a case, the number of moles of substance that decompose under definite conditions does not depend on the pressure. Also, in such a case, the value of the constant does not depend on the units used in the measurement of the pressure. When, however, the number of moles of gases occurring on one side of the chemical equation is not equal to the number of moles of gases occurring on the other side, not all the pressures can be canceled. In this more general case, the pressure has an effect on the mole fractions of the gases when equilibrium is reached, and the value of the constant depends on the pressure unit, though not on the pressure itself.

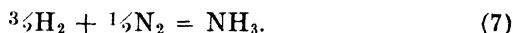
It is very important to note what we may vary and still leave unaffected the value of K_p . The temperature must not change, but the total pressure and the various partial pressures may be changed without affecting the value of K_p . Such changes of the partial pressures may be produced by starting our reaction with various mixtures of the reactants and products. We did not assume that we started in the above case with pure HI, or with equal numbers of moles of H_2 and I_2 ; we might start with a mixture of HI and H_2 , or even begin with a mixture containing an inert gas such as argon.¹ The equilibrium values of the partial pressures will differ accordingly, but must always be such as to satisfy the mass action equation, such as Eq. (6). The remarks in this paragraph apply, whether or not the number of moles of reactants equals the number of moles of products.

The value of K_p for the decomposition of hydrogen iodide, as written in Eq. (1), has been found by experiment to be about 0.020 at 448°. It is reasonably independent of the proportions of hydrogen and iodine taken and brought to equilibrium.

98. The Haber Equilibrium.—This affords an important illustration of a reaction in which the number of moles of products is not equal to the number of moles of reactants, but less. In this case an increase of pressure causes an increase in the theo-

¹ The inert gas will not contribute any terms to the mass action expression.

retical yield of ammonia obtainable, though it does not, according to the simple theory here given, which is based on the simple theory of gases, affect the value of the equilibrium constant K_p . The reaction is



The mass action expression is

$$\frac{(px)_{\text{NH}_3}}{(px)_{\text{H}_2}^{3/2}(px)_{\text{N}_2}^{1/2}} = K_p. \quad (8)$$

Canceling out the total pressure p as far as possible, we obtain the equation

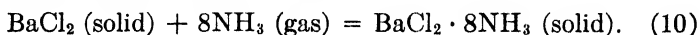
$$\frac{(x)_{\text{NH}_3}}{(x_{\text{H}_2})^{3/2}(x_{\text{N}_2})^{1/2}} = pK_p. \quad (9)$$

When we increase the pressure, K_p remaining constant, the mole fraction of ammonia in the equilibrium mixture must be increased, in order to satisfy Eq. (9). At the same time, the mole fractions of hydrogen and nitrogen are decreased, in accordance with Eq. (7). Thus an increase of pressure brings about a greater yield of ammonia as formed from the elements. In the various commercial processes for the fixation of nitrogen by means of the Haber equilibrium, from 200 to nearly 1,000 atm. are used. It is found in practice that K_p is somewhat increased by increasing the pressure, so that more benefit is obtained by increasing the pressure than would be expected from the simple theory.

99. Reactions Involving Solutions and Solids.—Turning now to reactions in solution, for instance in water solution, we may apply similar reasoning and reach a similar result. Since the partial molal free energy of a dissolved substance is $RT \ln c_1 + k_1$ in dilute solution, or more precisely and generally, $RT \ln a_1 + k_1$, where a_1 is the activity of a non-electrolyte or ion, the mass action law for dissolved substances is the same in outline as for gases, but concentrations or activities are inserted into the outline instead of partial pressures. The equilibrium constant is the value of the function. It depends on the temperature and on the pressure. The dependence on pressure is due to the small effect of pressure on vapor pressure and is itself small. The equilibrium constant depends also on the nature of the phase.

This has only lately been fully appreciated by chemists, who are finding it possible to improve yields in some cases by changing the nature of the medium in which the reaction is carried out, for instance, from a solution phase to a gas phase.¹

When we have occasion to write the mass action function for a reaction in which gases, solids, and solutions take part, we make full use of the proposition that the partial molal free energy of a given substance is the same in two phases in equilibrium. Thus to take a simple case, the equilibrium represented by the following equation can be studied:



The solids do not dissolve in one another. Their free energies will be given by expressions of the type $RT \ln x_1 + k_1$, where x_1 is the mole fraction of the substance in the solid, namely, unity. Since the logarithm of unity is zero, the free energies per mole of the solids are k_1 and k_2 . The free energy of ammonia per mole is $RT \ln p + I$. Substituting these values for the chemical symbols in Eq. (10) and changing all the signs, we have

$$-k_1 - 8RT \ln p - 8I = -k_2. \quad (11)$$

Here there is only one variable pressure and the 8 causes no real complication. We have

$$-\ln p = \ln \left(\frac{1}{p} \right) = \frac{(k_1 - k_2 + 8I)}{8RT}. \quad (12)$$

The expression on the right is constant at constant temperature and pressure,² and may be regarded as the natural logarithm of K_p , the equilibrium constant for the reaction (10). Hence

$$\ln (1/p) = \ln K_p,$$

or

$$1/p = K_p.$$

¹ The equilibrium constant for any phase can be calculated from that for another phase, if we know the Henry's law or distribution constants for all the substances concerned.

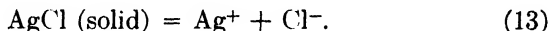
² K_p will in fact be constant at constant temperature, unless inert gases are present. In such a case it will vary slightly with the total pressure, and the partial pressure of ammonia will occur in the mass action function instead of simply the pressure.

When considering solids, it is unnecessary to go through the whole process each time. Simply write the partial pressures of the gases, and the concentrations or activities of the dissolved substances, in the mass action outline, and omit any terms relating to pure solids, as their free energies contribute only constants, which are included in the value of the mass action constant. The older chemists used to express this as follows: The active mass of a solid is constant.

If Eq. (10) is written in the reverse order, we have the equation for the decomposition of $\text{BaCl}_2 \cdot 8\text{NH}_3$ (barium chloride octamine). The mass action expression for the *decomposition* will have the pressure for ammonia in the *numerator*, since ammonia is a product of the reaction. Thus,

$$p = K_p.$$

100. Solubility Product.—When a solution containing silver or chloride ions is saturated with silver chloride, that is, brought to equilibrium with the solid, we have equilibrium with respect to the reaction



The mass action expression, omitting any term for the solid, is

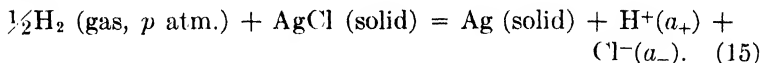
$$(\text{Ag}^+)(\text{Cl}^-) = K, \quad (14)$$

where the quantities in parentheses may represent concentrations or activities of the silver and chloride ions. The product on the left of Eq. (14) is called the solubility product. When activities are used, the solubility product is constant at constant temperature (and pressure), though the excess of silver or chloride ions in the solution may be greatly varied. The solubility of silver chloride is low, and if the concentration of the solution is not made too great in ions by addition of electrolytes like HCl or AgNO_3 in large excess, Eq. (14) will be valid in terms of concentrations. Suppose now a certain excess, not too great, of HCl is added to a solution of water saturated with pure silver chloride. The addition of chloride ions will then necessitate a reduction in the concentration of silver ions, so as to leave the solubility product the same as before. Hence the diminution of solubility observed on adding a small excess of chloride ion.

When the chloride ion is added, some cation is of course added at the same time, such as hydrogen ion. But the hydrogen ion does not enter the reaction (13) or the mass action equation (14), and is therefore without any direct effect on the solubility. It is the common (chloride) ion which has a direct effect, and the effect on the solubility of this kind is called the common ion effect.

When the concentration of the solution in ions is great, Eq. (14) will not be valid in terms of concentrations. Electrolytes without a common ion usually increase the solubility when they are present in large quantity.

101. Mass Action Constant and Electromotive Force.—Consider the following reaction:



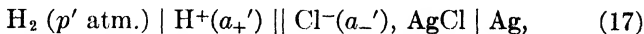
The product would be hydrochloric acid, but we arrive at the mass action relations for a strong electrolyte only by consideration of its ions, and in writing equations involving strong electrolytes we therefore represent them as completely ionized.¹

In writing the mass action expression corresponding to Eq. (15) we omit the solids, represent the gas by its pressure, and the ions by their activities a_+ and a_- . We have therefore

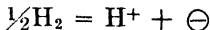
$$\frac{(a_+) \times (a_-)}{(p)^{\frac{1}{2}}} = K. \quad (16)$$

This equation must hold when the activities and pressure are for the substances when they are all present together in chemical equilibrium.

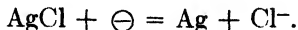
If we pass one faraday from left to right through the cell



we have the anode reaction,



and the cathode reaction,



¹ Remember that Raoult's and Henry's laws do not apply to the whole electrolyte.

The net result is given by the sum of these electrode reactions and is the same as in reaction (15), except that the hydrogen is used up at the pressure p' and the hydrogen and chloride ions are produced at the activities a_+' and a_-' , respectively, which are those as existing in the cell, and are in general different from those in the equilibrium mixture. The loss of free energy per faraday passed through the cell from left to right will be equal to E_F , where E is the electromotive force of the cell as written, and we have in the usual way,

$$E_F = \frac{1}{2}RT \ln p' + \frac{1}{2}I_{H_2} + k_{AgCl} - RT \ln a_+' - k_+ - RT \ln a_- - k_- - k_{Ag}. \quad (18)$$

For the chemical equilibrium the free energy change is zero, the pressure and activities being p , a_+ and a_- . We have then also

$$0 = \frac{1}{2}RT \ln p + \frac{1}{2}I_{H_2} + k_{AgCl} - RT \ln a_+ - k_+ - RT \ln a_- - k_- - k_{Ag}. \quad (19)$$

Subtraction of Eq. (19) from Eq. (18) serves to eliminate the I and k constants:

$$E_F = \frac{1}{2}RT \ln p' - RT \ln a_+' - RT \ln a_- - \frac{1}{2}RT \ln p + RT \ln a_+ + RT \ln a_-. \quad (20)$$

Rearrangement into more convenient form gives

$$E_F = RT \ln \frac{(a_+)(a_-)}{(p)^{\frac{1}{2}}} - RT \ln \frac{(a_+')(a_-')}{(p')^{\frac{1}{2}}}. \quad (21)$$

But this contains the natural logarithm of the equilibrium constant K [Eq. (16)], as well as the logarithm of a very similar expression, in which the pressure and activities are not equilibrium values, but the values for the substances as existing in the electrical cell. Let us call this similar expression K' . Equation (21) may then be more simply written

$$E_F = RT \ln K - RT \ln K', \quad (22)$$

where K is the mass action function of the equilibrium pressures and activities and K' is the mass action function of the values of the pressures and activities as existing in the cell. Equation (22) holds for any reaction taking place in a cell whose electromotive force is E , provided only that the chemical reaction for

which the mass action function is written expresses the result of passing one faraday through the cell.

In the present case the equilibrium has not been directly measured. From Eq. (22) and the appropriate molal electrode potentials the equilibrium constant K can be calculated. It is very large, over 5,000 (moles per kilo, atmospheres), indicating a strong tendency of the reaction (15) to proceed from left to right, and to produce either very large activities of hydrogen and chloride ions, or to leave but the smallest pressure of hydrogen gas.

Sometimes the electromotive force of a cell cannot be accurately measured, and then Eq. (22) can be used to calculate it from available measurements of chemical equilibrium. A number of molal electrode potentials given in tables, among them that for the oxygen electrode, were in fact found in this way.

If all the pressures and activities in the cell are the same as might exist in a mixture in chemical equilibrium, then in Eq. (22) $K = K'$, and $E = 0$. This condition may be approximately realized in some cells by short-circuiting the cell until it is completely discharged.

102. The Mean Activity of the Ions of a Strong Electrolyte.—Although concentrations may be used in Eq. (16) in place of activities, when the solution is sufficiently dilute, there is no need for doing this in the case of hydrochloric acid (and of many other) solutions, as the relationship between the concentration and the activity has been experimentally determined. When H^+ and Cl^- ions are transferred (or, in the case of the above cell, *formed*) together in the proportions present in HCl , the transfer is really one of HCl , and all we need to know is the activity for HCl , and we do not need the individual activities or activity coefficients of the separate ions.¹

It is well to know the custom followed in reporting activity data. Lewis and Randall define a mean activity of the ions of a strong electrolyte, a_{\pm} . Whenever the electrolyte in question ionizes into two ions of valence one, the mean activity a_{\pm} is defined to be equal to the square root of the product (a_+a_-).

¹ These latter do not need to be equal even in the same solution of pure HCl in water.

It is thus a geometric mean. In terms of this mean activity, Eq. (16) becomes

$$\frac{(a_{\pm})^2}{(p)^{1/2}} = K. \quad (23)$$

The activity coefficient for such a simple strong electrolyte, like HCl, is defined to be the number, designated by γ (gamma), by which the molality of the electrolyte in moles per kilo of water must be multiplied to get the mean activity. Then the exact equation, in terms of the molality m of the HCl, becomes

$$\frac{(m\gamma)^2}{(p)^{1/2}} = K. \quad (24)$$

Values of γ are given by Lewis and Randall¹ for 25°. A noteworthy illustration of the bad failure of the simple expression $RT \ln c + k$ for the ions in strong solutions is that the value of γ becomes greater than 1 at 2 molal, rising to 43 in the strongest solution. Below 2 molal, however, the error committed in assuming gamma equal to 1 (or that $RT \ln c + k$ is exact for the ions) would not exceed 28 per cent.

For electrolytes which dissociate into more than two ions, or into ions not all of valence one, more general (and complicated) definitions are given for the mean activity and the activity coefficient of the whole electrolyte.

103. Variations of Convention Regarding Activities.—We have related the activity to the partial molal free energy of a substance by stating that the latter is given by the expression $RT \ln a + k$. We must now explain, in order to prepare the student who may sometime seek to decipher equilibrium data as given in original papers in terms of activities, that not all authors adhere strictly to this relation at all times. We have seen that the I and k constants have a habit of being eliminated, or being combined with one another to give a single constant which must be determined by experiment. If we had in fact expressed the partial molal free energy by $RT \ln k'a + k$ we should have arrived always at the same results, for this equals $RT \ln a + (RT \ln k' + k)$, and the term in parenthesis is simply

¹ "Thermodynamics and the Free Energy of Chemical Substances," Table 4, p. 336.

another constant, which would have been eliminated or combined as before.

In the hands of an expert, it makes no difference whether he allows the extra k' or not; he will always reach the same end result. But his talk about activities will sometimes vary. Suppose he is considering the distribution of a substance between ether and water layers. Then, at equilibrium, the partial molal free energy of the substance is the same in the ether phase as in the water phase. But if for both phases we put the partial molal free energy equal to $RT \ln a + k$, the two values of k will not be the same, and therefore the activity of the substance will not be the same. Using subscripts to distinguish the two phases, we shall have

$$RT \ln a_1 + k_1 = RT \ln a_2 + k_2,$$

and therefore $\ln (a_1/a_2) = (k_2 - k_1)/RT$.

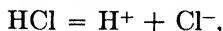
Let us denote the latter expression by $\ln k_3$. Then we shall have

$$a_1/a_2 = k_3, \quad (25)$$

or the activities of the substance in the two phases are proportional at constant temperature (and pressure). This is of course the distribution law in terms of activities.

The activities of any substance in various phases in equilibrium will always be at least proportional at constant temperature and pressure. But by modifying the first relation to $RT \ln k'a_1 + k_1$, we may in the above case make the activity of the substance the *same* in both phases; namely, by choosing k' equal to $k_2 - k_1$. Some writers like to define their activities occasionally so that the activities will not only be proportional in different phases, but also numerically equal.

A somewhat similar case is given by the equilibrium



representing the ionization of hydrochloric acid in aqueous solution. The partial molal free energy of HCl is equal at equilibrium to the sum of the partial molal free energies of H^+ and Cl^- . If expressions of the form $RT \ln a + k$ are used for all three activities, we find that the activity of HCl is proportional to the

product of the activities of H^+ and Cl^- , that is, that $a_{HCl} = (a_+a_-)$ times a constant. But by modifying the definition of the activity of HCl to $RT \ln k'a + k$, a value of k' can be found such that $a_{HCl} = a_+a_-$, or, in terms of the mean activity of the ions, $a_{HCl} = (a_{\pm})^2$. Lewis and Randall define a_{HCl} in this way for their Table 4, page 336.

104. The Ionic Strength.—The activity coefficient is found to depend very largely on the concentration of the solution in strong electrolytes, and on the valences of the ions present. A single quantity, the so-called *ionic strength*, has been found to represent rather well the combined effect of concentration and valence, so that the activity coefficient depends strongly on the ionic strength of the solution. This is defined to be one-half the sum of the quantities $m_1z_1^2$, for all the ions of the strong electrolytes present, where m_1 is the molality of the ion, in moles per kilo of water (under the hypothesis of total ionization for the strong electrolytes), and z_1 is the valence of the ion. Thus, for a solution containing 0.1 mole of HCl per kilo, the ionic strength will be

$$\frac{1}{2}(0.1 \times 1^2 + 0.1 \times 1^2) = 0.1,$$

the same as the molality. For a solution containing 0.1 mole of $BaCl_2$ per kilo, the ionic strength will be, however,

$$\frac{1}{2}(0.1 \times 2^2 + 0.2 \times 1^2) = 0.3.$$

Notice that the molality of chloride ion is twice that of barium ion. The ionic strength has been designated by the Greek μ .

Problems

1. Write the mass action expression (in terms of pressures) for the decomposition of calcium carbonate into calcium oxide and carbon dioxide.

2. (a) Write the mass action expression (in terms of partial pressures) for the formation of one mole of ammonia gas from the elements. (b) Is the mass action function of the mole fractions equal to that of the partial pressures?

3. (a) Show that the ionic strength of a solution containing 0.1 mole HCl , 0.05 mole $CaCl_2$, and 0.02 mole Na_2SO_4 per kilo of water is 0.31. (b) Find the ionic strength of a solution containing 0.2 mole each of sodium acetate and acetic acid per kilo of water. (Regard the acetic acid as undissociated.)

4. The value of K_p for the formation of one mole of ammonia gas from the elements at $500^\circ C.$ and at 1 atm. total pressure (and thereabout) is 0.00382,

when the pressure unit is the atmosphere. If, starting with pure ammonia gas, we decompose it at 500° until equilibrium is attained at a total pressure of 1 atm., what will be the volume percentage of ammonia in the equilibrium mixture?

Hints: The volume percentage will be practically equal to 100 times the mole fraction. Remember that the sum of the three mole fractions is unity, and that in this case the mole fraction of H_2 will be 3 times that of N_2 . By the use of algebra, find the value of the expression

$$\frac{x}{(1 - x)^2}$$

where x is the mole fraction of ammonia at equilibrium, and solve for x approximately, first putting the denominator equal to unity. Then improve the calculation if necessary by using a better value for the denominator obtained by the use of the first approximate value of x . *Ans.* 0.124 volume per cent.

CHAPTER XXI

TYPICAL APPLICATIONS OF THE MASS ACTION LAW IN TERMS OF CONCENTRATIONS TO ELECTROLYTES IN SOLUTION

We need not repeat henceforth that the mass action law, as applied to cases of chemical equilibrium, is always exact when activities are used in the mass action outline or function. A number of important types of problems can be solved with a sufficient degree of exactness, using concentrations in the function, and these will now be studied.

In this treatment we sharply distinguish between the weak and the strong electrolytes. We shall regularly apply the mass law to the ionization of weak electrolytes, taking account of the concentration of undissociated electrolytes, but in the case of strong electrolytes we shall never take account of any undissociated fraction, but shall assume the ionization to be complete. In the activity treatment, the same sharp distinction is observed, and the definitions are so made that the activity treatment parallels in many respects the approximate treatment in terms of concentrations.

105. The Ionization of Weak Monobasic Acids.—Let us first consider the ionization of a weak acid, such as acetic acid (HAc), when it is dissolved in water. The equation for the ionization is



The reaction is of course reversible, but it is helpful to write it in a definite direction, the products being on the right. Let us in our equations use parentheses to indicate concentrations, in moles per liter. The mass action law for the ionization is then

$$\frac{(\text{H}^+)(\text{Ac}^-)}{(\text{HAc})} = k, \quad (2)$$

where (HAc) represents the concentration of undissociated acid. No other solutes are supposed present, so that

$$(H^+) = (Ac^-).$$

Hence,

$$(H^+)^2 = k(HAc) \quad (3)$$

and k is a constant so long as the temperature is constant. We shall ignore the very small effect of pressure upon the value of k . The constant k is called the ionization constant or dissociation constant of the acid.

Suppose that c moles of acetic acid are mixed with enough water to make a liter of solution, and that the fraction ionized is α when the total concentration is c . Then the concentration of H^+ is $c\alpha$ moles per liter, that of Ac^- is the same, and the concentration of undissociated acid (HAc) is $c(1 - \alpha)$. Therefore the expression

$$c \frac{c^2 \alpha^2}{(1 - \alpha)} = \frac{c \alpha^2}{1 - \alpha} = k \quad (4)$$

follows from the mass action equation (2). Using the conductance ratio [see Chap. XII, Eq. (3)] for the fraction ionized, k is in fact found to be constant, as shown in Table I, in which the dilution is represented by the volume v that contains one mole of acetic acid.

TABLE I.—THE MASS ACTION CONSTANT FOR ACETIC ACID AT 25° FROM EARLY CONDUCTANCE DATA¹

v	8	16	32	64	128	256	512	1024
$10^3 k$	1.80	1.79	1.82	1.79	1.79	1.80	1.80	1.77

The average value of k is 1.8×10^{-5} at 25°. Deviations from this value are small and irregular, showing no definite trend with dilution.

When the conductance ratio is substituted for α in Eq. (4), and $1/v$ for c , the resulting equation is called Ostwald's dilution law.

¹ OSTWALD, *Z. physik. Chem.*, **3**, 170 (1889). The dissociation constant of acetic acid has very recently been discussed by Cohn, Heyroth, and Menkin, *J. Am. Chem. Soc.*, **50**, 696 (1928), as obtained from e. m. f. measurements, and interpreted by means of activity coefficients and the Debye-Hückel theory.

Similar results have been obtained with many weak monobasic acids and weak monacid bases. In the case of the weak monacid base, we may write the ionization equation, using M for any metal or metallic radical:



The mass action law is like the one for acids, except that OH^- occurs instead of H^+ .

Equation (3) may be used to calculate the hydrogen-ion concentration and hence the pH of a solution of a weak monobasic acid in water, if we know the quantity of acid dissolved and the value of the ionization constant. Let (acid) represent the number of moles of acid dissolved in a liter of solution. Then the concentration of undissociated acid (HA) will equal (acid) - (H^+) . Hence, from Eq. (3),

$$(H^+)^2 = k[(\text{acid}) - (H^+)]. \quad (6)$$

If we know (acid) and k , we can solve the quadratic equation for (H^+) . The best way to do this is to find first an approximate value of (H^+) from the equation

$$(H^+) = \sqrt{k(\text{acid})} \quad (7)$$

This approximation will usually be a very good one, as for weak acids the ionization is very small, so that (acid) - (H^+) is nearly equal to (acid). A better approximation may easily be obtained, if desired, by substituting the approximate value of (H^+) for the last term in Eq. (6), and then extracting the square root. It is well to remember Eq. (7), as it is almost always exact enough, and is very useful. Since it is the pH that will usually be desired, we may as well take logarithms before extracting roots. Thus,

$$pH = \frac{1}{2}[-\log k - \log (\text{acid})] \quad (8)$$

The quantity, $-\log k$, is commonly called the ionization constant of the acid expressed as a pH, and is designated by pK.

The hydrogen-ion concentration of a solution of a weak acid is greatly lessened on the addition of any soluble salt of the acid.

This is evident from Eq. (2). As stated above, we assume that the salt is completely ionized. Looking at Eq. (2) we see that the addition of sodium acetate, and therefore of acetate ions, to a solution of acetic acid must cause a decrease of H^+ ions, or an increase of undissociated HAc , or both. Naturally we shall have both a decrease of H^+ ions and an increase of HAc , in accordance with Eq. (1). Hence the concentration of undissociated acid (HAc) will be equal to (acid), the number of moles of acid originally dissolved in a liter of solution, to an even better degree of exactness than in the previous case and, furthermore, the concentration of acetate (Ac^-) will be practically equal to the number of moles of salt dissolved per liter, represented by (salt), in any solution in which any significant quantity of the salt is present, as the number of acetate ions from the acid will be very small. Making these substitutions for (HAc) and (Ac^-) in Eq. (2), we have

$$(H^+) = k \frac{(\text{acid})}{(\text{salt})}. \quad (9)$$

This approximate equation will hold for any weak monobasic

The student may wonder why we may still use the mass action expression for the acetic acid when sodium acetate is present. It is very important to note that the addition of new substances does not invalidate the mass action equations for the substances already present. This is because each mass action expression results from the fact that there is equilibrium in the system with respect to some chemical reaction. Now when the system is in equilibrium, it must be in equilibrium with respect to *each* separate reaction which we are considering. When we add new substances, there may be possible new chemical reactions, with new mass action expressions, but the mass action expressions which held for the old substances must still hold, unless the new substances happen to prevent the attainment of equilibrium, by poisoning any catalysts, or by acting as "anti-catalysts." The above remarks are strictly true for mass action expressions in activities, and hold for those in concentrations provided the added substances do not too greatly increase the total concentration of dissolved substances, especially of electrolytes.

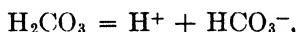
Similarly, for weak monacid bases dissolved in water together with a salt with a common ion, we shall have the approximate equation

$$(\text{OH}^-) = k_b \frac{(\text{base})}{(\text{salt})}, \quad (10)$$

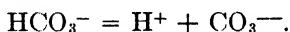
where k_b represents the ionization constant of the base. In the future, we shall write k_a for the ionization constant of an acid when we wish to distinguish.

Equations (9) and (10) are very important. We shall use them to explain the behavior of indicators. Often we may use them even for polybasic acids, or for polyacidic bases, but under special circumstances, as will be discussed.

106. The Ionization of Polybasic Acids.—A dibasic acid can ionize in two steps. For instance, carbonic acid, believed to be present in very small quantities in aqueous solutions of carbon dioxide, ionizes in the first step as follows:



and in the second step,

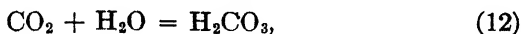


The ionization constant of the second step is almost always much smaller than that of the first step. When a third step is possible, as in the case of phosphoric acid H_3PO_4 , its constant is even smaller than that of the second step. It frequently happens that the difference in value of the constants is so great that we may need to consider only one step or the other at a time, according to the conditions (principally governed by the pH).

The true mass action constant for the first step of carbonic acid would be

$$\frac{(\text{H}^+)(\text{HCO}_3^-)}{(\text{H}_2\text{CO}_3)} = k_1, \quad (11)$$

where (H_2CO_3) represents the concentration of carbonic acid itself. But it is difficult to determine how much of the dissolved carbon dioxide is really H_2CO_3 and how much is simply dissolved CO_2 , and it is customary not to attempt this. The carbon dioxide reacts with water to form the acid, according to the equation



and the equilibrium is reached rather rapidly, though not instantaneously. The corresponding mass action expression may be written

$$\frac{(\text{H}_2\text{CO}_3)}{(\text{CO}_2)} = k_2(\text{H}_2\text{O}) = k_3. \quad (13)$$

For (13), we might put the vapor pressure of water, but for the dilute solutions to which our results must be limited this will be nearly constant at constant temperature, and therefore it is customarily "included" in the constant k_3 . Multiplication of the two constants k_1 and k_3 eliminates (H_2CO_3) , giving

$$\frac{(\text{H}^+)(\text{HCO}_3^-)}{(\text{CO}_2)} = k_1 k_3. \quad (14)$$

Solving Eqs. (11) and (14) for (H_2CO_3) and (CO_2) , respectively, and adding, we obtain

$$(\text{H}_2\text{CO}_3) + (\text{CO}_2) = (\text{H}^+)(\text{HCO}_3^-) \left(\frac{1}{k_1} + \frac{1}{k_1 k_3} \right),$$

or

$$\frac{(\text{H}^+)(\text{HCO}_3^-)}{(\text{H}_2\text{CO}_3) + (\text{CO}_2)} = \frac{1}{\frac{1}{k_1} + \frac{1}{k_1 k_3}} = k_4. \quad (15)$$

Comparison of Eq. (15) with Eq. (11) shows that we may use Eq. (11) with the understanding that (H_2CO_3) represents in it the total amount of dissolved carbon dioxide, whether present as such or as carbonic acid. The constant k_1 is then called an apparent dissociation constant. Its value is 3×10^{-7} at 18° .

The case for the weak base NH_4OH is similar, as we do not know how much of the dissolved ammonia has really reacted with the water. We write, however,

$$\frac{(\text{NH}_4^+)(\text{OH}^-)}{(\text{NH}_4\text{OH})} = k,$$

and regard k as an apparent constant, since all the dissolved ammonia will be assumed to be in the form NH_4OH when the formula is applied.

In some applications of the mass action law to carbon dioxide it is convenient to write the partial pressure of CO_2 , instead of

its concentration in the liquid. Thus, instead of Eq. (13) we should have

$$\frac{(\text{H}_2\text{CO}_3)}{p_{\text{CO}_2}} = k_3', \quad (16)$$

and instead of Eq. (14) we should have

$$\frac{(\text{H}^+)(\text{HCO}_3^-)}{p_{\text{CO}_2}} = k_1 k_3'. \quad (17)$$

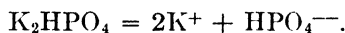
In these last two equations P_{CO_2} means of course the partial pressure of carbon dioxide in a gas in equilibrium with the solution.

The second ionization constant of carbonic acid is about 4.6×10^{-11} at 18° . This is far enough away from the first constant for us to ignore the second stage when the hydrogen-ion concentration of the solution is not far from 10^{-7} .

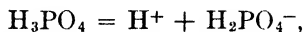
Let us examine in greater detail the various stages of ionization of phosphoric acid. Suppose we wish to calculate the pH of a solution at 18° made up by dissolving 0.1 mole KH_2PO_4 and 0.1 mole K_2HPO_4 in enough water to make a liter of solution. Assume the salts to be strong electrolytes, completely ionized according to the equations



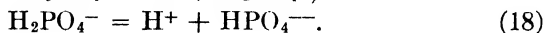
and



The equations for the first two steps of ionization of phosphoric acid are



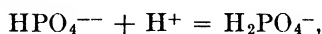
and



Now in the solution these two reactions may take place backwards to a certain extent, since the solution contains the necessary anions from the dissolved salts, and all aqueous solutions contain hydrogen ions as the result of the ionization of water. These two reactions will be subject to the two mass action expressions for the ionizations. Let us first consider the mass action expression for the second step, because both the added anions occur in it:

$$\frac{(\text{H}^+)(\text{HPO}_4^{--})}{(\text{H}_2\text{PO}_4^-)} = k_2. \quad (19)$$

The values for the three steps, k_1 , k_2 , and k_3 , were determined from mass action data, with the use of conductance data, as 1.1×10^{-2} , 2.0×10^{-7} , and 3.6×10^{-13} , respectively, at 18° .¹ These constants are considered to be far apart in value, as will shortly appear. Let us suppose first, as an approximation, that only the second-stage reaction,

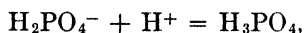


takes place. Then we may substitute in Eq. (19) for the ions, the number of moles per liter of the salts that furnish them, obtaining the provisional result:

$$(\text{H}^+) = \frac{0.1}{0.1} 2.0 \times 10^{-7} = 10^{-6.70},$$

or $\text{pH} = 6.70.$ (20)

But some of the H_2PO_4^- may have been used up in the reaction



which would make this result incorrect. To see what effect this reaction would have, let us examine the mass action expression

$$\frac{(\text{H}^+)(\text{H}_2\text{PO}_4^-)}{(\text{H}_3\text{PO}_4)} = 1.1 \times 10^{-2}. \quad (21)$$

Now, the concentrations (H^+) and $(\text{H}_2\text{PO}_4^-)$ are at least approximately fixed as 2.0×10^{-7} and 0.1, respectively. Substitution of these values into Eq. (21) gives the concentration of H_3PO_4 formed by the reaction

$$(\text{H}_3\text{PO}_4) = \frac{(\text{H}^+)(\text{H}_2\text{PO}_4^-)}{1.1 \times 10^{-2}} = \frac{2.0 \times 10^{-7} \times 10^{-1}}{1.1 \times 10^{-2}} = 2 \times 10^{-6}. \quad (22)$$

The concentration of H_3PO_4 is therefore negligible in comparison with that of the H_2PO_4^- added in the form of salt, so that no correction is necessary for loss of H_2PO_4^- by formation of H_3PO_4 .

Similarly, the ionization constant for the third step is so far removed from that of the second, that the concentration of PO_4^{---} ions formed by the ionization comes out to be only 1.8×10^{-7} , negligible in comparison with 0.1.

¹ Such data, determined without reference to activity coefficients, are to be found in the Landolt-Börnstein Tabellen.

The result we obtained for the pH of the solution was 6.70. Actual measurement gave 6.685, an excellent check. Agreements as good as this are not usually obtained and are not even in this case, if the best available value of k_2 (as obtained from pH measurements) is used. Fair results are to be expected, however, when the concentrations of the salts, and especially the ionic strength, are low, and when the ratio of the two salts dissolved to make the solution does not differ too greatly from unity.¹

This illustrates that when the constants for different steps of ionization are far enough apart in value, we need to consider only one step at a time, and the approximate calculation of the pH becomes really as simple as in the case of a monobasic acid. Calculations of this sort have a definite field of usefulness, in spite of the fact that the pH of solutions can in general be more exactly measured than calculated.

Our use of Eq. (19) for the calculation of the hydrogen-ion concentration of a solution prepared with primary potassium phosphate (KH_2PO_4) and the secondary phosphate (K_2HPO_4) can be summarized in the equation

$$(\text{H}^+) = k_2 \frac{(\text{prim.})}{(\text{sec.})}, \quad (23)$$

where (prim.) designates the number of formula weights of primary phosphate put into the liter of solution, and (sec.) the number of secondary phosphate. Noting that k_2 is the ionization constant for the ionization of primary phosphate anion, we see that this equation may be regarded as a special case of Eq. (9), in which primary phosphate is regarded as the acid, and secondary phosphate as the salt.

The following statement may be convenient for reference, when considering whether the constants for two adjacent steps of ionization are far enough apart to justify us in considering only one stage. If the ratio of the concentrations of the two substances as weighed out is not more than 10 or less than 0.1, then the error in considering only the one step will not exceed 1 per cent on the hydrogen-ion concentration (which corresponds to

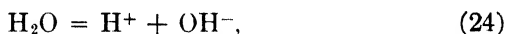
¹ A modern treatment of phosphate mixtures has been given by Cohn (see Clark's "The Determination of Hydrogen Ions"). His concentrations are in formula weights per liter.

an error of 0.004 pH), provided that the pK values of the ionization constants for the adjacent steps differ by as much as 3.

When the hydrogen-ion concentration is known, it is easy to calculate from equations such as (19) and (21) the ratios among the various forms in which the acidic substance, as PO_4 , is distributed. If we know also the total amount of the acidic substance, it is not difficult to find the concentration of each kind of anion, even if more than one stage must be considered at a time.

107. The Ionization of Water.—The specific resistance of pure water is very high, about 25 million ohms at 18° . Such pure water is seldom prepared, ordinary preparations of very pure water showing figures of from 10^5 to 10^6 ohms. The conductance of pure water is believed due to the ionization into H^+ and OH^- ions. From the mobilities of these two ions it is not difficult to calculate¹ that a concentration of about 10^{-7} gram ions of each of these two ions per liter would suffice to produce the low degree of conductance of the very purest water.

The equation for the ionization of water is written



and the corresponding mass action expression would be

$$\frac{(\text{H}^+)(\text{OH}^-)}{p_{\text{H}_2\text{O}}} = k. \quad (25)$$

In dilute solutions the vapor pressure (and the activity) of the water is nearly constant, so that $p_{\text{H}_2\text{O}}$ (or $a_{\text{H}_2\text{O}}$) is generally included in the mass action constant by writing

$$p_{\text{H}_2\text{O}}k = k_w.$$

We have then

$$(\text{H}^+)(\text{OH}^-) = k_w, \quad (26)$$

where k_w is the ionization constant, or, better, the *ionic product* of water. Since the concentrations of H^+ and OH^- are each about 10^{-7} , the ionic product of water is about 10^{-14} . Though it has been evaluated for a solution in which the H^+ and OH^- ions are equal, it must have the same value when they are not equal,

¹ Prob. 4, Chap. XII.

as in acid or alkaline solution, provided the solution is not too concentrated, especially in strong electrolytes.

Other methods are available for determining the value of the ionic product of water. These depend on the application of mass action equations involving it to experimental measurements of various equilibria. The ionic product, and therefore the degree of ionization, is found to increase rapidly with rising temperature. Table II gives some values, the uncertainties of which correspond to the variation produced by perhaps one or two degrees.

TABLE II.—THE IONIC PRODUCT OF WATER

Temperature, degrees Centigrade	0	18	25	37.5	100	300
k_w expressed as pK	14.9	14.2	14.0	13.6	12.3	11.4

The unit of concentration is the gram ion per liter of solution or per kilo of water. See "International Critical Tables," Vol. 6, p. 152 (1929) for complete tables and summary.

There are many applications of the mass action equation (26). We can immediately use it to get convenient equations for the pH of alkaline solutions.

108. The pH of Alkaline Solutions.—The hydroxyl-ion concentration of a solution of a strong base in water will be approximately equal to the number of gram equivalents dissolved in a liter of solution. Let this concentration be represented by (base). Then we have at once

$$(\text{H}^+) = \frac{k_w}{(\text{OH}^-)} = \frac{k_w}{(\text{base})}. \quad (27)$$

For a solution of a weak monacid base alone in water we find from reasoning similar to that used in deriving Eq. (7)

$$(\text{OH}^-) = \sqrt{k_b (\text{base})}, \quad (28)$$

and therefore

$$(\text{H}^+) = \frac{k_w}{\sqrt{k_b (\text{base})}}. \quad (29)$$

For a solution of a weak monacid base and a salt of that base we have from Eq. (10)

$$(\text{H}^+) = \frac{k_w (\text{salt})}{k_b (\text{base})}. \quad (30)$$

From these equations, which need not be memorized, the value of the pH in each case is easily found by taking logarithms. For instance, from Eq. (30) we should have

$$\text{pH} = -\log (\text{H}^+) = \log \frac{(\text{base})}{(\text{salt})} - \log k_w + \log k_b \quad (31)$$

$$\text{pH} = \log \frac{(\text{base})}{(\text{salt})} + \text{pK}_w - \text{pK}_b, \quad (32)$$

where pK_w is the ionic product of water expressed as a pH, and pK_b the ionization constant of the base expressed similarly.

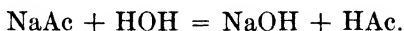
109. The Effect of Salts on the pH of Solutions.—We shall consider only the effects of adding relatively small quantities of salts, so that the ionic strength of the solution is not increased enough to make inaccurate the use of concentrations in place of activities.

Addition of a *neutral* salt does not affect the pH of any of the solutions mentioned above. A neutral salt is one produced by the reaction of a strong base with a strong acid (both acid and base having a single stage of ionization). Such a neutral salt in water furnishes only its ions; for example, NaCl gives Na^+ and Cl^- . A possible reaction with water to form NaOH and HCl would form H^+ and OH^- ions in equal concentrations, since the strong acid and base are equally ionized, and therefore the solution is neutral. Since, furthermore, there can be only one hydrogen-ion concentration in the same solution, and we must always have $(\text{H}^+) \times (\text{OH}^-)$ a constant, the concentrations of H^+ and OH^- are not only equal, but are equal to their concentrations in pure water.¹

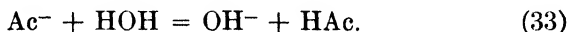
The reason why the addition of a neutral salt does not affect the hydrogen-ion concentration of any of the solutions discussed above is simply that none of the mass action equations involving it contain concentrations of ions such as Na^+ , K^+ , Cl^- , NO_3^- , etc., which belong to strong acids or bases. Let us not forget the principle that any given mass action expression holds by itself, independently of other mass action expressions, or of the presence in the solution of ions not represented in it.

¹ The pH of the solution of a neutral salt in water is practically equally sensitive to the addition of traces of acid or alkali as pure water itself.

A solution produced by dissolving in water a salt of a weak acid and a strong base is not neutral, but alkaline. Take sodium acetate as an example. We have the reaction taking place to a certain extent:



The sodium acetate and sodium hydroxide are both strong, and are assumed to be completely ionized. Therefore the Na^+ ions appear on both sides and do not take part in the reaction. Before writing the mass action equation we therefore rewrite the reaction in the ionic form



The mass action equation is

$$\frac{(\text{OH}^-)(\text{HAc})}{(\text{Ac}^-)} = k_h, \quad (34)$$

where k_h is the so-called hydrolysis constant, and includes the constant vapor pressure of water.

When the salt is alone in water, the production of hydroxyl ions by hydrolysis gives an alkaline solution. When the salt is added to an acid solution, the production of OH^- lowers the concentration of H^+ with the formation of water. In this case the hydrolysis continues until the concentration ratio $(\text{HAc})/(\text{Ac}^-)$ attains a value consistent with Eq. (34), with the value of k_w , and with the mass action expressions for the substances in the original acid solution.

Similarly, a solution produced by dissolving in water a salt of a weak base and a strong acid, such as ammonium chloride, imparts acidity to water, and the addition of the salt lessens the hydroxyl-ion concentration of an alkaline solution. Naturally, the effect on the hydrogen-ion concentration of a strongly acid solution will be negligible.

The effect of adding a little sodium acetate to a dilute solution of hydrochloric acid is easy to calculate. If (HCl) is the number of moles of HCl per liter before the addition of sodium acetate, and (NaAc) is the number of moles of acetate added per liter, then the reaction, $\text{HCl} + \text{NaAc} = \text{HAc} + \text{NaCl}$, which is, in the ionic form, $\text{H}^+ + \text{Ac}^- = \text{HAc}$, may be regarded as practically com-

plete in the presence of an excess of HCl, which furnishes a large value of (H^+) . The resultant concentration of hydrochloric acid, and hence of hydrogen ion, is then simply $(HCl) - (NaAc)$.

110. The Effect of Strong Acids or Bases on the pH of Solutions.

One example should suffice. Suppose we have a solution of sodium acetate in water in the concentration $(NaAc)$ moles per liter and add a small quantity of hydrochloric acid, namely, (HCl) moles per liter. Then the reaction $H^+ + Ac^- = HAc$ will take place, and since the hydrogen-ion concentration of mixtures of acetic acid and acetate is always very low, practically all the HCl will be used up in furnishing H^+ for this reaction, provided only that a reasonable concentration of acetate is left. Hence the concentration of HAc equals (HCl) , and the concentration of acetate left over is $(NaAc) - (HCl)$. Using Eq. (9), we have

$$(H^+) = k_a \frac{(\text{acid})}{(\text{salt})} = k_a \frac{(HCl)}{(NaAc) - (HCl)}, \quad (35)$$

where k_a is the ionization constant of acetic acid.

111. Hydrolysis.—We have given above in Eq. (34) the mass action expression which governs the hydrolysis of a salt of a weak acid and a strong base. Suppose we dissolve c moles of NaAc in one liter of water, what fraction of the NaAc will be hydrolyzed into NaOH and HAc? Let this fraction be α . Then the concentration of OH^- will be $c\alpha$ and (HAc) will also be equal to $c\alpha$, since the ionization of the weak acid is very slight. The concentration of sodium acetate left, and therefore of Ac^- , is $c(1 - \alpha)$. In terms of the fraction α , the mass action expression is therefore

$$\frac{c^2\alpha^2}{c(1 - \alpha)} = k_h = \frac{c\alpha^2}{(1 - \alpha)}. \quad (36)$$

Since the concentration c is not completely eliminated by cancellation, the fraction α must vary with the concentration c , to satisfy Eq. (36). In order that k_h remain constant, α must increase when c is decreased by dilution of the solution.

The constant k_h may thus be determined by measuring (OH^-) and c , since α equals $(OH^-)/c$. The concentration (OH^-) may be determined from a pH measurement if k_w is known.

Another way to determine k_h is as follows. Multiply the left-hand side of Eq. (34) by $(H^+)/(H^+)$. This gives

$$\frac{(H^+)(OH^-)(HAc)}{(Ac^-)(H^+)} = k_h = \frac{k_w}{k_a}, \quad (37)$$

where k_a is the ionization constant of the weak acid, equal to $(H^+)(Ac^-)/(HAc)$. The hydrolysis constant of a salt of any combination of a weak monobasic acid and a strong base is evidently given by

$$k_h = k_w/k_a. \quad (38)$$

This applies also to a salt of a polybasic acid with a strong base if the ionization constants are far enough apart.

By independent measurement of k_h , Eq. (38) has also been used in one method of calculating k_w . Finally, the equation has been used to calculate k_a from k_h and the known value of k_w in cases where it is difficult to determine k_a , as in the case of the second or third stage of ionization of polybasic acids.

If the salt is formed from a strong acid and a weak base, like NH_4Cl , we have the hydrolysis equation (in the ionic form)



The hydrolysis constant is

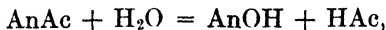
$$\frac{(NH_4OH)(H^+)}{(NH_4^+)} = k_h. \quad (40)$$

Multiplying the left-hand side by $(OH^-)/(OH^-)$, we have

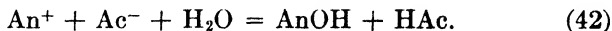
$$\frac{(NH_4OH)(OH^-)(H^+)}{(NH_4^+)(OH^-)} = \frac{k_w}{k_b} = k_h, \quad (41)$$

where k_b may be the ionization constant of any weak monacid base. The hydrolysis of such a salt increases with dilution in the same way as in the previous case.

If the salt is formed from a weak base and a weak acid, the hydrolysis is in general greater in extent, and the equations present a novelty. Take as an example aniline acetate, which we may write $AnAc$. The hydrolysis equation might be written,



where AnOH represents aniline,¹ but we shall obtain the customary hydrolysis equation only by writing it in the ionic form, considering the salt to be completely ionized:



The mass action expression is

$$\frac{(\text{AnOH})(\text{HAc})}{(\text{An}^+)(\text{Ac}^-)} = k_h. \quad (43)$$

If we dissolve c moles of aniline acetate in one liter of solution, and if the fraction of it which is hydrolyzed is α , then the concentration of AnOH produced is $c\alpha$, and likewise for (HAc) . The concentration of salt not hydrolyzed is $c(1 - \alpha)$, and this is therefore the concentration of aniline cations, and also of acetate anions. We have then

$$\frac{c^2\alpha^2}{c^2(1 - \alpha)^2} = k_h = \frac{\alpha^2}{(1 - \alpha)^2}. \quad (44)$$

Since the concentration is here completely eliminated by cancellation, and the result holds, whatever the original value of c , therefore the fraction hydrolyzed is independent of the concentration, so long as the solutions are not so strong as to require activity corrections.

Again, multiplying the left-hand side of Eq. (43) by $k_w/[(\text{OH}^-)(\text{H}^+)]$, we have

$$\frac{(\text{AnOH})(\text{HAc})}{(\text{OH}^-)(\text{An}^+)(\text{Ac}^-)(\text{H}^+)} k_w = k_h, \quad (45)$$

or

$$k_h = k_w/k_b k_a. \quad (46)$$

The hydrolysis constant k_h may be calculated, by the use of Eq. (46), for any salt of a weak acid and a weak base, provided they are, or act like, a monobasic acid and a monacid base, from the values of the ionization constants of the acid and base and the ionic product of water.

¹ Aniline is $\text{C}_6\text{H}_5\text{NH}_2$. In water solution it acts like a base, as if it had a formula such as $\text{C}_6\text{H}_5\text{NH}_3\text{OH}$. Thus An^+ is $\text{C}_6\text{H}_5\text{NH}_3^+$.

Comparing the expressions for k_h —namely, k_w/k_a , k_w/k_b , and $k_w/k_a k_b$ —we see that the last expression will generally be greater than the two others, since all the k 's are small fractions. The fraction hydrolyzed increases with k_h , and hence the degree of hydrolysis is relatively great when both acid and base are weak. Table III shows the percentage of hydrolysis when 0.1 equivalent of various salts is dissolved in water per liter of solution, at 25°. The values are for illustration, and are not necessarily the best available values.

TABLE III.—PERCENTAGE OF HYDROLYSIS AT 25° AND 0.1 NORMAL OF SOME SALTS

Salt	Per cent	Salt	Per cent
Sodium acetate.....	0.008	Potassium cyanide.....	1.2
Ammonium chloride.....	0.006	Aniline hydrochloride. ...	1.6
Ammonium acetate.....	0.37*	Sodium carbonate.....	2.9
Borax.....	0.5	Aniline acetate.....	50

* Measured at 20°.

It is a well-known fact that no endpoint can be obtained if we try to titrate a weak acid with a weak base, or *vice versa*. Considering aniline and acetic acid as an example, we can see why this is so, by examining Eq. (42) for the hydrolysis. The hydrogen ion does not appear in this equation, so that the extent of the hydrolysis is independent of the hydrogen-ion concentration [within the wide limits of applicability of Eq. (43)]. Naturally then, no pH value can be found for the solution that will make the neutralization [the reverse of Eq. (42)] complete. On the other hand, a weak acid like acetic acid can be titrated with a strong base, and hydrolysis does not prevent an endpoint, though it has an effect on the pH value of the solution when the endpoint is reached. The mass action expression for the hydrolysis was given as Eq. (34):

$$\frac{(\text{OH}^-)(\text{HAc})}{(\text{Ac}^-)} = k_h.$$

When (OH^-) is increased by adding a strong base, the ratio $(\text{HAc})/(\text{Ac}^-)$ must be decreased so as to keep k_h constant. By

adding enough base, (HAc) may be made negligible in comparison with (Ac^-), or, in other words, practically all the acid may be converted into salt. Unless the acid is extraordinarily weak, this will be accomplished before any large value of (OH^-), which would correspond to an appreciable excess of free base, is reached.

112. On the Errors Tolerated in Calculations of Hydrogen-ion Concentration.—The physical chemist strives for a precision of about 0.1 per cent in measuring or calculating the hydrogen-ion concentration or activity, when working in pure physical chemistry. Thus he looks askance at approximate calculations in which concentrations are used in place of activities, and regards with some suspicion the measurement of electromotive force of cells containing a liquid junction whose potential is of doubtful value (even when a salt bridge is used). The effects of varying pH are however rather coarse grained, whether these effects relate to the growth of bacteria, the action of enzymes, the precipitation of colloids, or even the solubility of relatively simple chemical substances. Hence a precision of 0.1 per cent in the hydrogen-ion concentration is not necessary for the ordinary biological or biochemical purposes. Let us consider the relation of pH to hydrogen-ion concentration.

When the hydrogen-ion concentration is 2×10^{-5} the pH is 4.7; when it is 10^{-5} , the pH is 5.0. Thus a *decrease* of hydrogen-ion concentration of 50 per cent, or an *increase* of 100 per cent of its value, causes a difference of only 0.3 in the pH value. Now in much biological and biochemical work it was found sufficiently precise to vary the pH by steps of 0.3. In Clark and Lub's buffer mixtures the interval of 0.2 pH was chosen. In using such mixtures for the colorimetric determination of pH by indicators, errors of 0.1 pH are frequent, and errors of 0.2 possible, due solely to the difficulty of color matching. From the definition of pH we have

$$-\log (\text{H}^+) = \text{pH}. \quad (47)$$

Suppose the correct pH is x , then $(\text{H}^+) = 10^{-x}$. If our measurement of pH gives $x - 0.1$, the calculated value of (H^+) will be 1.26×10^{-x} , since the log of 1.26 is 0.1; thus the hydrogen-ion concentration found is 26 per cent too great. It is interesting to

find the corresponding error in millivolts of the electromotive force of a cell for the determination of pH. The value of $RT/0.4343F$ is about 59 millivolts, but depends somewhat on the temperature. From Eq. (12) of Chap. XIX (page 160) we have therefore

$$E = 0.059(\text{pH}_1 - \text{pH}_2) \text{ volts.} \quad (48)$$

This is the electromotive force of two half cells at pH_1 and pH_2 , and is therefore the difference in the electromotive force of any cell when one of its half cells at pH_1 is replaced with one at pH_2 . When the difference of pH is 0.1, the difference of E is therefore about 5.9 millivolts. The physical chemist seeks often a precision of 0.1 or even 0.01 millivolt, but the biologist may often be pleased with a precision of 1 millivolt, which corresponds to a precision of about 0.017 pH.

On account of these relations, the approximate treatment of the mass action law in terms of concentrations has been very useful to the biologist, and the usefulness promises to persist for a long time to come.

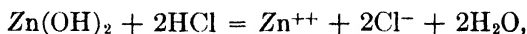
Problems

1. A solution is made 0.1 *N* with acetic acid and 0.1 *N* with sodium acetate at 25°. What is the pH?
2. 200 cc. of 0.1 *N* acetic acid and 100 cc. of 0.1 *N* NaOH are mixed and made up to a volume of one liter at 25°. What is the pH?
3. Calculate the pH of a solution containing 0.05 formula weight of primary sodium phosphate and 0.025 formula weight of secondary sodium phosphate at 18°.
4. A solution at 18° contains primary and secondary sodium phosphates, sodium bicarbonate (NaHCO_3), and dissolved carbon dioxide. If there is an equal number of moles of primary and secondary phosphates in the solution, what is the ratio of the concentration of total dissolved carbon dioxide divided by the concentration of bicarbonate?
5. The ionization constant of NH_4OH at 25° is about 1.8×10^{-5} . Find the pH of a solution 0.04 *N* in NH_4OH and containing no ammonium salts.
6. Using this value for NH_4OH and the other necessary constants as given in the text, find (a) the hydrolysis constant of ammonium acetate at 25° and (b) the percentage hydrolysis in a dilute solution at 25°. Hint: do not worry about $(1 - \alpha)^2$; it is nearly equal to unity, and may be so taken.

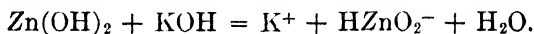
CHAPTER XXII

AMPHOTERIC ELECTROLYTES

In elementary chemistry we learn that zinc hydroxide can dissolve in acids to form zinc ion, as



or in strong alkalies to form a zincate, as



Substances like zinc hydroxide which can form either cations or anions are called *amphoteric electrolytes*, or *ampholytes*. Many organic substances act in this way, especially the amino-acids, of which a simple type may be represented as $\text{NH}_2\text{—R—COOH}$, where R denotes some organic radical. (If R is CH_2 , we have amino-acetic acid, also called glycocoll and glycine.) Such an ampholyte can dissociate into $\text{NH}_2\text{—R—COO}^- + \text{H}^+$, or can react with water to form $\text{OH}^- + \text{NH}_3\text{—R—COOH}^+$. For the greater brevity, let us write HAmOH for the ampholyte when undissociated, AmOH^- for the anion, and HAm^+ for the cation.

113. Mass Action Relations.—Now the two possible modes of ionization are independent, and we shall have the two following mass action expressions holding independently:

$$\frac{(\text{H}^+)(\text{AmOH}^-)}{(\text{HAmOH})} = k_a, \quad (1a)$$

$$\frac{(\text{OH}^-)(\text{HAm}^+)}{(\text{HAmOH})} = k_b. \quad (1b)$$

From these equations it may be seen that in acid solutions there will be relatively little of the ampholyte in the form of anions, since when (H^+) is large, Eq. (1a) shows that the ratio $(\text{AmOH}^-)/(\text{HAmOH})$ must be relatively small, and Eq. (1b) shows that the ratio $(\text{HAm}^+)/(\text{HAmOH})$ must be relatively large, and also

the concentration of cations. Similarly, in alkaline solutions more of the ampholyte will be present as anions than as cations. In short, the ampholyte acts like a base in acid solutions, and like an acid in alkaline solutions.

In solutions of intermediate pH the ampholyte ionizes both ways. A very interesting result is obtained by applying Eqs. (1) together. Solving them for (AmOH^-) and (HAm^+) , respectively, and adding to get the total concentration of all ampholyte ions, both anion and cation, we have

$$(\text{AmOH}^-) + (\text{HAm}^+) = (\text{HAmOH}) \left[\frac{k_a}{(\text{H}^+)} + \frac{k_b}{(\text{OH}^-)} \right]. \quad (2)$$

Since in any solution (H^+) increases as (OH^-) decreases, the factor in brackets varies with (H^+) or with the pH, and it can be shown by the use of a little calculus, that the factor in brackets will have a minimum value when

$$(\text{H}^+) = \sqrt{k_a k_w / k_b}, \quad (3a)$$

i. e.,

$$\text{pH} = \frac{1}{2}(\text{p}K_a - \text{p}K_b + \text{p}K_w). \quad (3b)^1$$

Therefore the sum of the concentrations of the ions of the ampholyte will be a minimum, that is, the ampholyte will be least ionized, at the pH given by this relation (3b). By substituting the value of (H^+) given by Eq. (3a) for the minimum into Eqs. (1), it will be found that the concentrations of both cation and anion of the ampholyte are equal at this pH, and equal to k_b/k_w .

At this pH we may say that the ampholyte has no net charge. When an electric current is passed through such a solution, the ampholyte does not migrate definitely towards either cathode or anode, since the mobilities of anion and cation are nearly the same. This is in contrast to the definite migration observed

¹ Take the factor in brackets, and differentiate with respect to (H^+) its equal: $\frac{k_a}{(\text{H}^+)} + \frac{k_b(\text{H}^+)}{k_w}$. Putting the derivative equal to zero to find the location of the maximum or minimum, we have $\frac{-k_a}{(\text{H}^+)^2} + \frac{k_b}{k_w} = 0$, which is essentially Eq. (3a). To find out whether it is a maximum or a minimum, we take the second derivative, and find it to be $+2k_a/(\text{H}^+)^3$. Since this is positive, there is a minimum, rather than a maximum.

when the ampholyte is predominantly anion or cation. Such a pH is called therefore the *isoelectric point* of the ampholyte.

At the isoelectric point the solubility of the ampholyte is less than at other values of the pH on either side; that is, the solubility is a minimum. This is easily seen from the result found above that the total concentration of ampholyte ions is a minimum at the isoelectric point. For the dissolved ampholyte consists of undissociated substance and of the ions. And the solubility of the undissociated substance is independent of the pH. This is because by solubility we mean the concentration when the solution is in equilibrium with the solid substance. The activity of the undissociated substance in solution is proportional to that of the solid, and since this is constant during the experiment (at a definite constant temperature), the activity of the undissociated ampholyte in solution is constant. Therefore the concentration of the undissociated ampholyte in the solution is constant, within the accuracy expected when using concentrations rather than activities. The total solubility varies then only with that due to the ions and is least at the isoelectric point.

The sharpness of the minimum of the solubility curve depends on the product $k_a k_b$; the larger this is, the greater the curvature of the curve at the minimum.¹ Sharply defined minima are observed in many instances, as in the cases of phenylalanine and para-aminobenzoic acid. In the case of casein, the minimum is extremely broad.²

Not only chemically definite amphoteric electrolytes show an isoelectric point and a minimum in the solubility curve, but also various proteins, colloids, and suspensions of bacteria and other biological material. In the case of suspensions we are hardly dealing with a true solubility, and what is observed is a difference in the time of settling out. Thus, when typhoid bacilli are thickly suspended in solutions of different pH but of nearly the same salt concentration (or, better, of the same ionic strength), they are found to settle out rapidly at a pH of about 4.4, and at higher and lower pH values they settle out more slowly or not at all in a reasonable time. This is called *acid agglutination*.

¹ When the solubility is plotted against the pH, the curvature at the minimum is proportional to the square root of $k_a k_b / k_w$.

² This applies to casein as ordinarily prepared.

Naturally, our equations need not apply exactly to such cases, or even to chemically definite ampholytes, unless these are of the simple type assumed, with only two ionizable groups. Often the minimum solubility is not exactly at the isoelectric point. Nevertheless, the equations furnish an interesting explanation of the behavior of more complicated cases, as long as we do not expect too much accuracy of the equations.

The interested student is referred for further discussion and examples to Leonor Michaelis' "Hydrogen Ion Concentration," translated by Perlzweig.¹ Michaelis has performed many interesting and important experiments in this field.

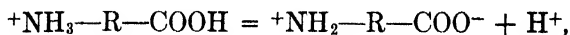
114. Hybrid Ions.—We have formulated the mass action law for ampholytes, supposing that the undissociated molecule has a chemical constitution of the type, $\text{NH}_2\text{-R-COOH}$, as ordinarily taught in organic chemistry. Considerable evidence was presented by E. Q. Adams in 1916 and by Bjerrum in 1923² to show that in many cases the so-called amino-acid has really a saltlike nature in water solution and a constitution better represented by $^+\text{NH}_2\text{-R-COO}^-$. Such a species, having at the same time a positive and a negative charge, is called a hybrid, or hermaphroditic ion (in German, *Zwitter-ion*). Since the net electrical charge is zero, it does not migrate in the electrical field. Experiments indicate that the substance behaves more like a salt (a so-called *inner salt*) than like a non-electrolyte, with respect to deviations from the mass action law in terms of concentrations.

They reformulate the mass action expressions in accordance with the assumption that the undissociated form is a hybrid ion. The general results are in most respects equivalent to those afforded by the usual formulation as given above, but the values of the ionization constants found by them meet the expectations of the organic chemist much better. Thus, k_a as we have formulated the ionization is about $10^{-9.75}$ for amino-acetic acid, whereas k_a for acetic acid is about $10^{-4.73}$. Now the substitution of a "negative" radical such as NH_2 ought to increase the value of k_a , since this is always observed of negative radicals when they

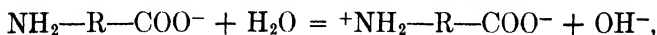
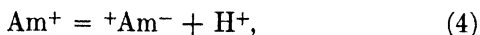
¹ The Williams and Wilkins Company, Baltimore, 1926.

² ADAMS, E. Q., *J. Am. Chem. Soc.*, **38**, 1503 (1916); BJERRUM, NIELS, *Z. physik. Chem.*, **104**, 147 (1923).

do not complicate the picture by imparting basic groups to the acid, and instead of an increase we see here a large decrease in k_a . Bjerrum's equations for the ionizations are



or



or



The mass action constants for these ionizations can be computed from the values of k_a and k_b as calculated according to the former formulation from the experimental data. If the mass action constants for reactions (4) and (5) be designated by K_A and K_B , respectively, the relations given by Bjerrum are

$$K_A = k_w/k_b \text{ and } K_B = k_w/k_a \quad (6)^*$$

The mass action constant for the reaction (4) is then, according to Adams and Bjerrum, the ionization constant for the carboxyl group ($-\text{COOH}$), and its numerical value comes out $10^{-2.33}$, which meets much better the expectation of the organic chemist.

Bjerrum estimates that over 99.5 per cent of the undissociated substance is in the form of hybrid ion in the case of the aliphatic amino-acids, from 90 to 10 per cent in the case of aromatic amino-acids (in which the radical R contains a benzene ring), and none in the case of the amino-phenols.

Equations (4), (5), and (6) lead back to the same result—Eq. (3) for the pH at which the solubility is a minimum—so that our previous results are not invalidated or affected numerically by the occurrence of hybrid ions.

* These follow from a simple comparison of the mass action expressions for K_A and k_b , and a similar comparison for K_B and k_a , remembering that (HAMOH) and ($^+\text{Am}^-$) are equal, being two different representations of the same concentration of amino-acid or other ampholyte.

CHAPTER XXIII

BUFFERS AND TITRATION CURVES

The effectiveness of enzymes, the growth and activity of microorganisms, the behavior of indicators and of colloids, and many biological phenomena depend greatly on the pH of the solution or medium, and in laboratory experimentation substances known as buffers are often added to such solutions or media in order to provide an environment of constant and known pH. The buffer must have the property that the pH of the fluid to which it is added does not change much when water is added to it, or even when a little acid or base is added or is present in the original solution.

115. Buffer Mixtures.—The equations of Chap. XXI enable us to discover what kinds of substance may act as buffers, and when.

For a solution of a strong acid we found the approximate equation

$$(\text{H}^+) = (\text{acid})$$

or

$$\text{pH} = -\log (\text{acid}), \quad (1)$$

where (acid) denotes the number of equivalents of acid dissolved in water to make a liter of solution. On diluting such a solution with an equal volume of water the hydrogen-ion concentration is evidently halved, and the pH is therefore increased by 0.3 ($= \log 2$), for we have

$$(\text{H}^+) = \frac{1}{2} (\text{acid}),$$

and

$$\text{pH} = -\log (\text{acid}) - \log \left(\frac{1}{2}\right) = -\log (\text{acid}) + \log 2.$$

On neutralizing one-half of the acid with a strong base such as NaOH, instead of adding water, the concentration of acid is halved, and the pH increased again by 0.3, since the sodium

chloride formed has no effect on the pH except that due to changing somewhat the activity coefficients.

For a solution of a weak acid in water the equation is

$$(\text{H}^+) = \sqrt{k_a(\text{acid})},$$

or
$$\text{pH} = -\frac{1}{2} \log (\text{acid}) - \frac{1}{2} \log k_a. \quad (2)$$

On diluting this solution with an equal volume of water the hydrogen-ion concentration is only divided by the square root of 2, and the pH increased by only 0.15. On neutralizing one-half of the acid with NaOH we shall have, however, a great increase of pH, as we must now use the equation

$$(\text{H}^+) = k_a \frac{(\text{acid})}{(\text{salt})}$$

or
$$\text{pH} = \text{p}K_a + \log \frac{(\text{salt})}{(\text{acid})}, \quad (3)$$

in which we must substitute the value of the concentration of acid left, and of salt formed. For reasonable values of the concentrations, Eq. (3) always gives a much smaller value of (H^+) than does Eq. (2), as, when k is a small fraction, k is much smaller than its square root. Such a solution of weak acid in water would not therefore be suitable for controlling the pH of biological fluids, since they usually contain substances capable of acting as acids or bases or both.

On the other hand, a solution of a weak acid already partially neutralized, say one-half, may be quite suitable. According to Eq. (3), the effect on the pH of merely adding water is zero, as the salt and acid are equally diluted, and only their ratio enters the equation. The measured effect is actually small. As to the effect of adding NaOH—suppose the solution originally has its acid half neutralized, so that the ratio, $(\text{salt})/(\text{acid})$, equals unity.

Then

$$\text{pH} = \text{p}K_a,$$

a result which should be carefully noted for its own sake. If we now add enough NaOH to use up half of the remaining acid, the ratio, $(\text{salt})/(\text{acid})$, is now $(\frac{3}{4} \div \frac{1}{4})$, that is, 3, so that the pH

is now $pK_a + \log 3$, or $pK_a + 0.48$. This change of 0.48 pH is not much greater than the effect, 0.3 pH, of half neutralizing a strong acid. Furthermore, we do not expect to lose half of the acid present by such neutralization by base present in the original solution, and when the fraction lost is small, the combination of weak acid plus salt is changed practically as little in pH as a solution containing the same quantity of a strong acid, provided the ratio of salt to weak acid has a value of unity.

If the ratio of salt to acid is, however, $\frac{1}{10}$ or $\frac{1}{1}$, the effect of half neutralizing the acid present will be to make the ratio $\frac{6}{5}$ or 10.5/0.5. Corresponding to the greater effect on the ratio there will be a greater effect on the pH of half neutralizing the acid present, whenever the original value of the ratio differs from unity. In practice, it is undesirable to make up buffers with the ratio, salt to acid (or base to salt, in the case of alkaline buffers), greater than 10 or less than 0.1.¹

In order to obtain a stable pH it is of prime importance to have in the solution as much acid substance as is consistent with other requirements. Chief of these requirements is that the pH must have a certain chosen value. If this is for instance $pH = 2$, then a strong acid may be (and in fact must be) used. If this is $pH = 5$, a strong acid is unsuitable, since its concentration would have to be 10^{-5} normal, so dilute that the solution would be entirely neutralized by an accidental trace of basic substance, and such traces are always present in the solutions and even on the surface of glassware. Evidently when the desired pH is about 5, we must use a weak acid plus salt, choosing an acid whose pK value is about 5, such as acetic acid. We may use a solution say 0.05 normal in acetic acid and about 1.8×0.05 normal in sodium acetate, thus using about 5,000 times as much acetic acid as would be permissible of hydrochloric acid, and obtaining a correspondingly more stable pH.

¹ Of course we may, in case of necessity, increase the total concentration of acid or of salt in order to get stability of pH with an extreme ratio. If, however, it is the salt which we wish to increase, we should take care that the ionic strength of the solution is not made too great. If, also, we are using the equations for monobasic acids for substances that are really di- or tri-basic, we may not be able to calculate the pH when the ratio is extreme, although this will not trouble us if it happens that we wish only to stabilize, and are willing to measure the pH rather than to calculate it.

It will be noted that when weak acids (or bases) are used, it is not only necessary to have sufficient acid present to take care of basic impurities or additions, but also necessary to have enough of the salt present to take care of the small quantities of strong acid¹ that may get into the solution. The properties of the combination as a buffer are best when the concentration ratio, weak acid to salt, or weak base to salt, is unity.

We may hardly say of acid or basic substances that some are buffers and some are not, but may say that *at a definite pH* some substances (or pairs of substances) are buffers and others are not. Thus, at a pH of 5, acetic acid plus acetate constitutes a buffer, but hydrochloric acid does not; and at a pH of 7, neither of them acts as a buffer, the hydrochloric acid being wholly neutralized, and the acetic acid too nearly so. Around a pH of 7 we may use the combination of primary and secondary phosphates, for instance, NaH_2PO_4 and Na_2HPO_4 , since the constant for the ionization $\text{H}_2\text{PO}_4^- = \text{H}^+ + \text{HPO}_4^{--}$ is about 7, corresponding to a ratio of about unity for the concentrations primary to secondary, at a pH of 7. For alkaline solutions, we may use weak bases plus their salts, and then weak bases alone if forced to do so. For biological work we do not in general need to pass to strong bases, as even moderately alkaline solutions are damaging to living substance and even to dead protein.

A considerable number of buffer mixtures have been prepared and their pH values measured, some of which values cannot easily be calculated from mass action expressions. For biological applications it is desirable that all the buffer mixtures of a series should have the same salt concentration, or, better, be made of equal ionic strength.

116. Titration Curves and Buffer Index.—The buffer action of a solution can be most clearly described by means of a titration curve. Figure 37 shows the changes of pH when 10 cc. of a standard solution of acetic acid is titrated with various quantities of equivalent standard sodium hydroxide solution. The first additions of base cause a considerable increase of pH. The effect on the pH grows less when about 5 cc. of base has been added, then becomes greater, until at about 10 cc. the pH changes

¹ Or of strong base, when we are considering the case of weak base plus its salt.

greatly. The sudden change at 10 cc. constitutes an endpoint, and if an indicator is present, the color of which changes within the interval of pH covered by the sudden change, its color will be seen to change greatly on the addition of a drop or two of base. It should be noted that the endpoint is present whether the indicator is present or not. If an unsuitable indicator is used, like methyl red, which undergoes its characteristic color change

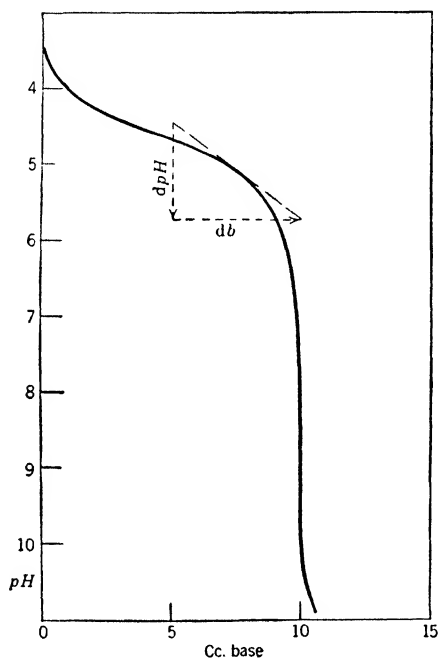


FIG. 37.—Titration curve for 10 cc. of a solution of acetic acid.

from pH 4 to 6, the color will change but slowly with addition of base to acetic acid, because the pH is changing but slowly from pH 4 to 6, and the endpoint will not be observed. With an indicator changing at about a pH of 7 the relations will be better, though not yet satisfactory for the purposes of analysis. If the curve is drawn on a very much enlarged scale, an especially steep portion of the curve is found at a pH of about 9 to 10, where phenolphthalein exhibits its color changes, and this indicator

is suitable for precise analytical titration. There are cases, such as the titration of acetic acid with ammonia, where there is no good endpoint on the titration curve, and no indicator can be found or invented which will permit a good titration.

Now, at 5 cc., where the acetic acid is half neutralized, the change of pH per cubic centimeter of added base is least. It is here that the buffer, or stabilizing, action is greatest. The buffer action is measured by the *rate* at which base is added to produce a unit increase of pH. This rate is greatest when the pH is changing the least. On the above curve the buffer action is greatest at 5 cc. and least at 10. This rate may be calculated from an experimentally determined curve by drawing a tangent to the curve at the desired point, as shown by the broken line of Fig. 37. The dotted lines then represent the differentials, db and dpH . The buffer action is given by the ratio of the lengths of these lines, db/dpH . When the quantity of base added along the line db is expressed in gram equivalents per liter of solution examined, the ratio db/dpH is called the *buffer index*. The buffer index is the same for 2 cc. of a solution as for 1 cc. The total buffer index of a solution is equal to the sum of the buffer indices due to various substances in it. The buffer index may equally well be determined by adding *acid* to a solution and measuring the resultant *decrease* of pH. It will then be interpreted as $-db/(-dpH)$, or as $da/(-dpH)$, where a is the number of equivalents of acid added, per liter of solution examined.

The middle of the steep drop in the curve of Fig. 37 at 10 cc. does not correspond to pH of 7, but is somewhat on the alkaline side of 7. When hydrochloric acid is titrated, the steep increase of pH begins at a higher acidity, and the pH changes rapidly over a greater pH range. Consequently any one of many indicators may be used to determine the endpoint when it is titrated with a strong base. When hydrochloric acid is titrated with ammonia, the steep drop in the curve begins at the higher acidity, but does not continue so far as even pH of 7; an endpoint can nevertheless be observed by the use of a suitable indicator, such as methyl orange or methyl red.¹

¹ A chemist would not of course titrate HCl with ammonia, but would titrate NH_4OH with HCl or some other strong acid. The relations are however the same, whichever way the titration is conducted.

When phosphoric acid is titrated, a rather steep increase of pH occurs when the first hydrogen is replaced, and a distinct increase when the second is replaced. From the figure on page 38 of Clark's "The Determination of Hydrogen Ions," the middle of the first increase is about $\text{pH} = 4.6$, and of the second, 9.3. By using two different indicators in succession, both hydrogens may be titrated successively. Such is not always the case with polybasic acids, as the ionization constants for adjacent stages may lie too close together.¹ This usually happens with inorganic polybasic acids, and more seldom with organic polybasic acids.

117. A Mathematical Proof.—It is a simple matter to show from the mass action theory in terms of concentrations that when a weak acid is progressively neutralized by a strong base the buffer action is greatest at the point where the acid is half neutralized, and where therefore the ratio (acid)/(salt) equals unity.

From Eq. (3) we have by substitution of natural logarithms for easy differentiation

$$\text{pH} = \text{pK}_a + 0.4343 \ln (\text{salt}) - 0.4343 \ln (\text{acid}). \quad (4)$$

Differentiation gives

$$d\text{pH} = 0.4343 d(\text{salt})/(\text{salt}) - 0.4343 d(\text{acid})/(\text{acid}). \quad (5)$$

But the increase db of strong base added equals the increase, $d(\text{salt})$, of salt produced, and also equals the decrease, $-d(\text{acid})$, of acid produced. Hence,

$$d\text{pH} = 0.4343[db/(\text{salt}) + db/(\text{acid})]. \quad (6)$$

This gives

$$db/d\text{pH} = \frac{1}{0.4343 \left[\frac{1}{(\text{salt})} + \frac{1}{(\text{acid})} \right]}; \quad (7)$$

$$db/d\text{pH} = \frac{(\text{salt})(\text{acid})}{0.4343[(\text{salt}) + (\text{acid})]}. \quad (8)$$

¹ The hydrogen may be replaced even when little sign of the replacement is seen on the titration curve. Thus, acid potassium phthalate is easily prepared in the solid state, but when it is formed by addition of KOH to phthalic acid solution, very little evidence of the formation is seen in the titration curve.

During the neutralization of the definite quantity of acid originally taken, the sum, (salt) + (acid), is constant, and therefore db/dpH will be a maximum when the product, (salt) (acid), is a maximum. When the sum of two numbers is constant, for example equals 6, the product of them is greatest when they are equal, as $3 \times 3 = 9$, $4 \times 2 = 8$, $5 \times 1 = 5$, etc. Hence the product, (salt) (acid), and hence the buffer action db/dpH is greatest when (salt) = (acid), that is to say, when the original acid is half neutralized. This can of course also be shown by differentiation of sa with respect to s , subject to $s + a = k$. We have

$$d[s(k - s)] = (k - s - s)ds$$

from which

$$d(sa)/ds = k - 2s.$$

Equating this to zero,

$$s = \frac{1}{2}k,$$

and

$$s = a.$$

The second derivative is

$$d^2(sa)/ds^2 = -2,$$

which is negative, showing that there is a maximum and not a minimum.

CHAPTER XXIV

INDICATORS

An indicator for titration of acid or base or for pH determination is a substance which exhibits in solution a color depending on the pH of the solution. It must necessarily have acidic or basic properties. The color of a *perfect* indicator would depend, at a given temperature, on nothing but the concentration of indicator in the solution and on the pH. It would have sufficient coloring power so that the pH of the solution would not be appreciably changed by the amount of indicator which must be added to produce a characteristic coloration. Many good indicators exist, of high coloring power, and whose color depends chiefly on the pH and the concentration of indicator.

118. Indicator Measurements of pH with Buffer Mixtures.—Given a series of good indicators, and a series of buffer mixtures of progressively different pH values—and these may readily be made up from prescriptions to be found in the standard books, such as that of Clark—the determination of pH by the use of indicators is a simple matter. We may take a portion of the “unknown” solution and find by trial which of our indicators is suitable. That indicator is suitable whose color in the solution is intermediate between the color produced in more acid solutions and the color produced in more alkaline solutions. From tables we find over what range of pH the color changes take place for this indicator, or find this out for ourselves with the aid of our buffer mixtures. We select a number of buffer mixtures covering this range, placing a certain volume (say 5 cc.) of each in a separate test tube. We add a suitable number of drops of the indicator to each test tube, and the same number of drops to an equal volume (5 cc.) of the unknown solution. By comparing colors, we find which buffer solution has the same color, and therefore the same pH, as the unknown.

Since the color of indicators usually depends somewhat on the ionic strength of the solution, the ionic strength of the buffers

should all be the same, and, if possible, the same as that of the unknown. But the ionic strength of the unknown is itself usually unknown. The investigator does the best he can, and in important cases should report, not only the pH found, but also the temperature, the indicator and buffer mixtures used, and whatever information he may have about the ionic strength of the unknown, or its concentration in salts.

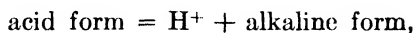
Some samples to be tested may have so little buffer action that the pH changes when the indicator is added. Such is the case with water when it is too nearly pure. The experimenter may then half neutralize his indicator solutions,¹ and may furthermore decrease the concentration of indicator added, making up the color by looking lengthwise through a long tube.

Means are discussed below for the case of unknowns which have a natural color.

119. The Theory of Indicators.—The behavior of nearly all the modern indicators may be explained, as regards the principal features, by assuming that they are monobasic acids which show one color when undissociated, and another when ionized to form anions. The hypothesis is due to Ostwald. We may write the ionization as



The form of the indicator present in quite acid solutions is evidently HIn, and the form present in quite alkaline solutions is evidently In⁻. We may therefore represent the ionization as



and the mass action law gives us

$$\frac{(\text{H}^+)(\text{alkaline form})}{(\text{acid form})} = k_a, \quad (1)$$

or

$$(\text{H}^+) = k_a(\text{acid form})/(\text{alkaline form}), \quad (2)$$

where the parentheses indicate concentrations.

¹ In the case of the strong dibasic sulphone-phthaleins, this means to add 1.5 equivalents of base per equivalent of indicator acid taken for the preparation of the stock solution of indicator.

It is sometimes convenient to represent the fraction of the indicator present in the alkaline form by the symbol α , then $1 - \alpha$ is the fraction remaining in the acid form. We have then

$$(\text{H}^+) = k_a(1 - \alpha)/\alpha, \quad (3)$$

or

$$\text{pH} = \text{pK}_a + \log \frac{\alpha}{(1 - \alpha)}. \quad (4)$$

This equation is very important in the theory of indicators. In order to see how the fraction present in the alkaline form varies with the pH of the solution, let us calculate the pH corresponding to various values of the fraction α , when the indicator used is methyl red, the pK of which is about 5.0. The steps in the calculation are given in Table I.

TABLE I. — THE RELATION BETWEEN THE FRACTION α AND THE pH

α	$1 - \alpha$	$\log \alpha$	$\log (1 - \alpha)$	$\log \frac{\alpha}{(1 - \alpha)}$	pH
		-1 +	-1 +		
0.1	0.9	0	0.954	-0.954	4.05
0.15	0.85	0.176	0.929	-0.753	4.25
0.2	0.8	0.301	0.903	-0.602	4.4
0.3	0.7	0.477	0.845	-0.368	4.6
0.4	0.6	0.602	0.778	-0.176	4.8
0.5	0.5	0.699	0.699	0	5.0
0.6	0.4	0.778	0.602	+0.176	5.2
0.7	0.3	0.845	0.477	0.368	5.4
0.8	0.2	0.903	0.301	0.602	5.6
0.85	0.15	0.929	0.176	0.753	5.75
0.9	0.1	0.954	0	0.954	5.95

In this table the pH values have been rounded off. Observe that in the middle of the table, from $\alpha = 0.2$ to 0.8 , a variation of 0.1 , or 10 per cent, in the fraction corresponds to a nearly constant variation of about 0.2 pH. But when α varies from 0.8 to 0.9 , the change of pH is much greater, about 0.35 , and the equation shows that to make α equal to 100 per cent the pH would have to be infinite. This means that no possible value of the pH could make α equal to 100 per cent, or to zero.¹

¹ The logarithm of zero is minus infinity.

Figure 38 shows the curve obtained by plotting α against the pH. The middle of the curve may be approximately represented by a straight line, and the ends of the curve never touch zero or 100 per cent.

The color of the solution containing the indicator in a definite total concentration depends principally on the value of α . Consequently, the color does not vary much when α varies from 0.9 to 0.99, though the pH in this case would vary from 5.95 to 6.99. Accordingly, the useful range of an indicator should be limited to a region of about 10 to about 90 per cent transformation into the alkaline form, or to a pH range of about 1.9. In practice the ordinary useful range, obtained without changing the concentration of total indicator, is only about 1.6. This

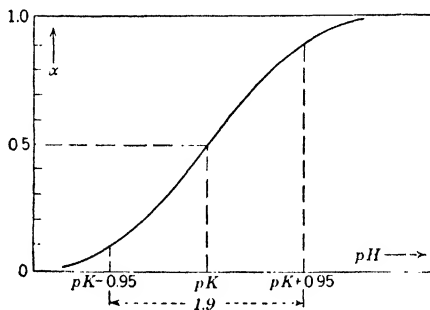


FIG. 38.—Fraction α of indicator transformed, plotted against the pH.

is principally due to the operation of a general biological law (law of Weber), that the physiological effect is not proportional to the physical cause, but increases much more slowly, in fact (according to Fechner) nearly as the logarithm of the cause. Consequently, when we have a red indicator in three tubes, in which it is respectively 60, 70, and 80 per cent transformed into the red form, we may see a considerably greater color in the 70 per cent tube than in the 60 per cent tube, but the 80 per cent tube is not much redder than the 70 per cent tube. If for some reason we must use this indicator, we can improve matters by using less indicator in all the tubes. When a two-colored indicator is used, the color of one is usually more intense (in equal concentration) than the other. The useful range then generally lies somewhat on the pH side toward which the con-

centration of the less intense form is increased. Thus, methyl red is intensely red on the acid side, and weakly yellow on the alkaline side of the 50 per cent transformation point. The useful range lies about from 4.4 to 6.0, more than half on the alkaline side of 5.0, when the total concentration of indicator has its best average value. By varying this total concentration appropriately, a little can be gained at either end.

The curves for other indicators that act like monobasic acids, such as the important series of sulphone-phthaleins, have precisely the same shape as shown in Fig. 38. Since their pK values are different, the curves would not coincide if plotted on the same diagram, but would be displaced horizontally, according to the value of the pK . In every case the curve cuts the horizontal line $\alpha = 0.5$ at a pH equal to pK .

A large number of indicators have been studied, whose pK values differ in such a way as to make most reasonable values of pH included in the range of one or more indicators. Some of these indicators, like thymol blue, have two useful ranges. The substance acts like a dibasic acid with ionization constants so far apart that one ionization is practically completed before enough alkali has been added to make the other ionization appreciable. This is generally true of the sulphone-phthaleins. The well-known phenolphthalein differs, being dibasic, but having its constants so near together that Eq. (4) does not apply, even approximately.¹

A one-colored indicator may be regarded as a special case of two-colored indicators, one of the colors being so faint as to be inappreciable. No special theory is therefore required for it. Two-colored indicators have the advantage, that when one color is decreasing the other is increasing. This usually makes the color changes more perceptible. Since colorimeters have been put on the market for two-colored indicators, they appear preferable to one-colored indicators in every respect.

120. Indicator Measurements without Buffers.—If we know that an indicator follows Eq. (4), and know its pK value, we may determine the pH of an unknown without the use of buffers. Suppose a certain indicator, when placed in the solution, is 40 per cent transformed into the alkaline form. Then we can obtain

¹ This makes no difference unless we wish to use it without buffer mixtures.

a color match with a tube of unknown solution plus indicator by observing the color through two tubes, one made acid, and

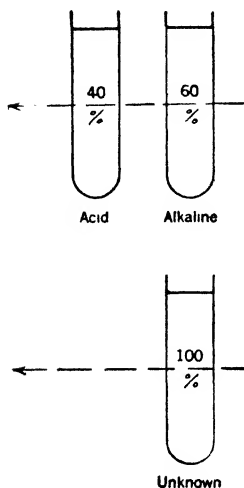


FIG. 39.—Determination of the percentage transformation of an indicator.

one made alkaline, all tubes having the same diameter. The acid tube must contain 60 per cent as much indicator as the unknown, in equal volume, and the alkaline tube, 40 per cent. The color as viewed through the two tubes should then match that seen through the unknown (Fig. 39). In the great dilutions in which modern indicators are used (about 10^{-4} normal) we may assume that light is absorbed independently by the two forms of the indicator, and hence the absorption of light, and in consequence of this the residual color emerging, will be the same whether the two forms are present together in the same (unknown) solution, or whether the forms are separated in two different vessels and the light passes through one vessel after the other.

Thus pairs of test tubes may be used in place of buffers. From Table I we see that it will be convenient to divide the total amount of indicator into tenths as shown in the scheme of Table II.

TABLE II.—PARTITION OF INDICATOR FOR STANDARDS WITHOUT BUFFERS

Alkaline tube receives.....	1	2	3	4	5	6	7	8	9
Acid tube receives.....	9	8	7	6	5	4	3	2	1
Corresponds to $\alpha =$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9

The parts may be 1 drop each. The unknown then receives 10 drops of indicator, and the volume is made the same in all tubes. The corresponding values of the pH vary by steps of 0.2 pH, except at the end, as a reference to Table I will show. Practical details are reported in Clark's "The Determination of Hydrogen Ions." However, it should be noted that in making the indicator solutions acid or alkaline, not enough acid or alkali

should be added to produce a "secondary" color change, that is, to make the pH such that some stage of ionization, other than that desired, is reached. In some cases it is necessary to use a weak acid or a weak base to produce the full acid or alkaline color.¹

121. Compensation for Natural Color of the Unknown Solution.—When the unknown is naturally colored, a simple expedient will serve to eliminate its effect, provided that the color is not too deep. It is simply necessary to place a tube of the unknown, without indicator, in the same path of light which traverses the standards (Fig. 40). The tubes of water are added to the optical paths to make a better color match possible. If light is again absorbed independently by the various substances, this mode of compensating for the natural color of the unknown will succeed, except in the improbable event that the indicator reacts chemically with the colored body. This procedure also compensates to a great extent for turbidity of the unknown.

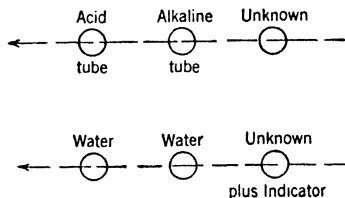


FIG. 40.—The pH determination of a colored solution without buffers.

122. Salt Errors of Indicators.—In the presence of too great a concentration of salt, especially salts of higher valences, the use of concentrations in mass action expressions instead of activities will not be quite correct. The percentage transformation will then determine the concentrations, but not quite determine the activities, as the activity coefficients for the colored bodies may not be the same in all solutions to be compared. But the color observed on looking through the solution depends on the concentration, rather than on the thermodynamic activity. Therefore the concentration ratios may be made equal without making the activity ratios of the indicator forms equal, and therefore without making the activity of hydrogen ion the same in the solutions for which a color match has been obtained. If the salt concentration of the unknown solution is approximately known, a correction may be made to the results obtained in the

¹ When the percentage transformation is about 95, the color may be considered practically the same as that which would correspond to 100 per cent.

usual manner, provided the salt correction has been studied for the indicator in question.

There are other ways in which the activity correction may enter. We have assumed that the indicator has the two forms, HIn and In^- . It can be shown, that the same general Eq. (4) will hold, even if the situation is complicated in all of the following ways: (1). In^- may exist in two tautomeric forms, only one of which needs to be colored.¹ Unless the tautomeric change is slow, no trouble will ensue. (2) Similarly, HIn may exist in two tautomeric forms, only one of which needs to be a colored substance. (3) The indicator may not be an acid at all, but a weak monacid base, with or without tautomeric complications. An application of the mass action theory in terms of concentrations shows that Eq. (4) will still hold in the face of any or all of these complications. The interpretation of the constant k_a will of course be different, but for the application of Eq. (4) we do not require a correct interpretation of k_a , but merely its value. When the ionic strength of the solution is so great, however, that the use of concentrations in the mass action expressions is too erroneous, activities should be used. By multiplying each concentration by an activity coefficient the corresponding activity is obtained. But every new isomer in question has an activity coefficient, which is usually not known, and which may vary from solution to solution.

¹ Two substances having the same composition and molecular weight, but different constitutions, are called isomers. When the chemical change from one isomer to the other takes place readily, an equilibrium usually being observed, the isomers are then called tautomers, and the chemical change is called the tautomeric change.

CHAPTER XXV

DONNAN EQUILIBRIUM, MEMBRANE AND INTERFACIAL POTENTIALS

In cases of ordinary chemical equilibrium, the partial molal free energy of any substance must be the same in any two phases in which it is present, when the phases are in equilibrium with respect to transfer of the substance from one phase to the other. But this is only true when the transfer of substance is free to take place. If the transfer of substance is conditioned by the flow of electrical current, and therefore accompanied by the doing of electrical work,¹ the partial molal free energy is not the same in two phases at equilibrium, and the difference is according to Gibbs equal to the electrical work done in the transfer.²

When, by the use of a semipermeable membrane, the transfer of some large ion is prevented, the transfer of other ions is no longer quite free, even though they are capable of passing through the membrane. This leads to peculiarities in the conditions of equilibrium.

123. Donnan Equilibrium.—The following experiment was performed by Donnan and Harris.³

A parchment paper membrane containing Congo red and sodium chloride in water solution was dipped into a solution of sodium chloride, and diffusion allowed to take place (Fig. 41). The parchment is (reasonably) impermeable to Congo red, but sodium chloride and other simple electrolytes can diffuse through it rapidly. When equilibrium was reached it was found that more sodium chloride was present per liter in the outside solution than in the inside solution. The mass action law predicts this.

¹ Or upon the rise or fall of the substance in a gravitational field, and therefore accompanied by the doing of gravitational work.

² Or gravitational work.

³ DONNAN, F. G., and A. B. HARRIS, *J. Chem. Soc. London*, **99**, 1554 (1911). See a recent general article by Donnan, *Chem. Rev.* **1**, 73 (1924), and Michaelis, "Hydrogen Ion Concentration."

The sodium chloride is free to diffuse. Although, as will be seen later, the ions are not separately free to diffuse, a sodium ion is certainly free to diffuse if accom-

panied by a chloride ion—thus, the salt itself is free to diffuse. At equilibrium, the partial molal free energy of sodium chloride must therefore be the same in both solutions. Let a_{Na} and a_{Cl} be the activities of Na^+ and Cl^- outside, and a'_{Na} and a'_{Cl} be the activities inside the parchment bag.

Then since from Chap. XV the partial molal free energy of an ion is given by $RT \ln a + k$, we must have at equilibrium

$$RT \ln a_{\text{Na}} + k_{\text{Na}} + RT \ln a_{\text{Cl}} + k_{\text{Cl}} = RT \ln a'_{\text{Na}} + k_{\text{Na}} + RT \ln a'_{\text{Cl}} + k_{\text{Cl}}. \quad (1)$$

The k constants may be canceled and then the RT , leaving

$$\ln a_{\text{Na}} + \ln a_{\text{Cl}} = \ln a'_{\text{Na}} + \ln a'_{\text{Cl}},$$

or

$$\ln (a_{\text{Na}} a_{\text{Cl}}) = \ln (a'_{\text{Na}} a'_{\text{Cl}}). \quad (2)$$

Therefore,

$$a_{\text{Na}} a_{\text{Cl}} = a'_{\text{Na}} a'_{\text{Cl}}. \quad (3)$$

This is the form taken by the mass action law when applied to this case. In words, the product of the activities of the ions of the sodium chloride must have in each solution the same value at equilibrium. Observe that it does not state whether or not the activity of either ion is the same on both sides of the membrane.

Considering dilute solutions, and assuming that the activity of an ion is equal to its concentration, we can easily show that the concentration of neither ion can be the same on both sides in the experiment with Congo red. Using concentrations for activities, we have

$$(\text{Na}^+)(\text{Cl}^-) = (\text{Na}^+)'\text{Cl}^-)', \quad (4)$$

where the parentheses indicate the concentrations of the ions. Now the Congo red in the inside solution is the sodium salt of an

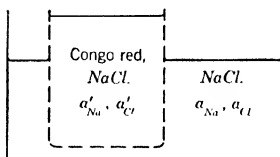


FIG. 41.—Illustrating notation for the Donnan equilibrium.

organic acid, which we may represent by Na_2R , and conductivity measurements showed this salt to be strongly ionized. Hence, in the inside solution there must be more sodium ions than chloride ions, enough to take care of the R^{--} ion as well as the Cl^- ion. Indeed, if $(\text{R}^{--})'$ is the concentration of R^{--} ions in equivalents per unit volume, we must have, for electrical neutrality of the inside solution,

$$(\text{Na}^+)' = (\text{Cl}^-)' + (\text{R}^{--})' \quad (5)$$

and for neutrality of the outside solution,

$$(\text{Na}^+) = (\text{Cl}^-). \quad (6)$$

It is now evidently impossible that the sodium-ion concentration should be the same in both solutions, or that the chloride-ion concentrations should be the same. For, if the concentrations of one are equal, inside and outside, then this must also be true of the other, by Eq. (4). Hence the sodium-ion concentration inside must be the same as the chloride-ion concentration inside (as they are equal in the outside solution), and this is by Eq. (5) impossible. There must be electrical neutrality.

Furthermore, from Eqs. (4) and (6) we have

$$(\text{Na}^+)'\text{(Cl}^-)' = (\text{Na}^+)^2 = (\text{Cl}^-)^2. \quad (7)$$

By Eq. (5), the concentration of sodium ions inside, $(\text{Na}^+)'$, must exceed that of chloride ions inside, $(\text{Cl}^-)'$. Hence, to satisfy Eq. (7), $(\text{Na}^+)'$ must exceed (Na^+) , and $(\text{Cl}^-)'$ must be less than (Cl^-) , as the square root of the product of two quantities must be intermediate in value between the two quantities.

Due to the presence of the non-diffusible R^{--} ions, the inside solution is thus weaker in chloride ion and stronger in sodium ion, than the solution outside. The concentration of sodium chloride is in each case the same as that of chloride ion, so that the inside solution is weaker in sodium chloride than the solution outside. This is what was found by experiment for the relations at equilibrium.

The relations may be made clearer by considering a possible state of affairs when equilibrium is reached, as given in Table I.

TABLE I.—SOME POSSIBLE CONCENTRATIONS OF THE IONS AT EQUILIBRIUM WHEN A SEMIPERMEABLE MEMBRANE IS USED

Kind of ion.....	R ⁻⁻	Na ⁺	Cl ⁻
Concentration inside.....	5	9	4
Concentration outside	0	6	6

The numbers give the concentrations, which might be taken as millimoles per 100 cc. From Table I we note that $(\text{Na}^+)(\text{Cl}^-) = 6 \times 6 = 36$ outside, and $(\text{Na}^+)'\text{Cl}^-)' = 4 \times 9 = 36$ inside, satisfying Eq. (4). There is neutrality inside, as $9 = 5 + 4$, and also outside, as $6 = 6$, satisfying Eqs. (5) and (6). Computed as salts, there are five equivalents per unit volume of Congo red salt and four of sodium chloride inside, and six of sodium chloride outside.

The ionic ratio $(\text{Na}^+)'/(\text{Na}^+)$, or $(\text{Cl}^-)/(\text{Cl}^-)'$, is $\frac{9}{6}$, or $\frac{3}{2}$, equal to 1.5 in the above case. This ratio is important in determining the membrane potential, as will be seen in the next section; the larger the ratio, the larger the potential. The ratio is larger, when the salt concentration is made smaller, or the Congo red concentration made larger. In Table II the effect of diminishing the sodium chloride concentrations is exhibited.

TABLE II.—SOME POSSIBLE CONCENTRATIONS IN A DONNAN EQUILIBRIUM WHEN LESS SODIUM CHLORIDE IS PRESENT

Kind of ion	R ⁻⁻	Na ⁺	Cl ⁻
Concentration inside.....	5	6.035	1.035
Concentration outside.....	0	2.5	2.5

The ionic product for sodium chloride outside is $2.5 \times 2.5 = 6.25$, and inside is $6.035 \times 1.035 = 6.246$, the same, within the precision of the figures given. The figures satisfy the condition of electrical neutrality. The ionic ratio is 2.414 or 2.415, larger than in the previous case.

In the experiment it was observed that the solution outside became alkaline, and the solution inside became acid. That is

to say, the concentration of OH^- ions was greater outside than inside, just as was the case for chloride ions, and the hydrogen ions behaved like the sodium ions. Hence we should consider these ions in the theory. Since both H^+ and Cl^- ions are present, HCl is free to diffuse. Therefore an equation like Eq. (3) must apply to its ions:

$$a_{\text{H}}a_{\text{Cl}} = a'_{\text{H}}a'_{\text{Cl}}. \quad (8)$$

The same is true for the ions of NaOH :

$$a_{\text{Na}}a_{\text{OH}} = a'_{\text{Na}}a'_{\text{OH}}. \quad (9)$$

From Eqs. (3), (8), and (9) we have

$$\frac{a'_{\text{Na}}}{a_{\text{Na}}} = \frac{a_{\text{Cl}}}{a'_{\text{Cl}}} = \frac{a'_{\text{H}}}{a_{\text{H}}} = \frac{a_{\text{OH}}}{a'_{\text{OH}}}. \quad (10)$$

This equation is easily extended to any number of ions of valence one that happen to be present, and we see that the ionic ratio will be the same for any univalent ion, if when writing the ratios we place the primed concentration or activity of cations in the numerator and of anions in the denominator of the ratio.

Taking account of the hydrogen and hydroxyl ions, some possible values have been calculated for a Donnan equilibrium and are given in Table III.

TABLE III.—SOME POSSIBLE CONCENTRATIONS IN A DONNAN EQUILIBRIUM, TAKING ACCOUNT OF THE IONS OF WATER

Kind of ion	R^{--}	Na^+	Cl^-	H^+	OH^-
Concentration inside	5	6.035	1.035	1.55×10^{-7}	0.65×10^{-7}
Concentration outside	0	2.5	2.5	0.65×10^{-7}	1.55×10^{-7}

From Table III the ionic products for water are about 1×10^{-14} , and the ionic ratios are 2.38, which agrees with those for sodium and chloride ions, 2.41, within the precision given for the concentrations of H^+ and OH^- . For electrical neutrality inside, R^{--} might be taken as 5.0000009 instead of 5, and microscopic corrections might be applied to the figures for Na^+ and Cl^- in the solution outside.

It is clear that the previous discussion, in which no consideration was given to the ions of water, was accurate enough for its purposes.

When, in the experiments of Donnan and Harris, the outside solution was replaced with pure water from time to time the loss of alkali caused a formation of free Congo red acid, or an acid salt, accompanied by clouding of the solution and precipitation. This was termed membrane hydrolysis.

124. Modifications of the Theory for Polyvalent Ions.—In the foregoing discussion only ions of valence one were considered. Let us now consider a sulphate ion, of valence two. It will be free to diffuse if accompanied by two hydrogen ions. The partial molal free energy of sulphuric acid must therefore be the same on both sides of the membrane. We must have

$$2RT \ln a_{\text{H}} + 2k_{\text{H}} + RT \ln a_{\text{SO}_4} + k_{\text{SO}_4} = 2RT \ln a'_{\text{H}} + 2k_{\text{H}} + RT \ln a'_{\text{SO}_4} + k_{\text{SO}_4}. \quad (11)$$

Hence,

$$\ln a_{\text{H}} + \frac{1}{2} \ln a_{\text{SO}_4} = \ln a'_{\text{H}} + \frac{1}{2} \ln a'_{\text{SO}_4}, \quad (12)$$

or

$$(a_{\text{H}})(a_{\text{SO}_4})^{1/2} = (a'_{\text{H}})(a'_{\text{SO}_4})^{1/2}. \quad (13)$$

Finally,

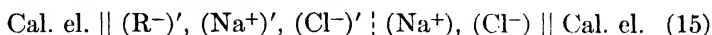
$$\frac{a'_{\text{H}}}{a_{\text{H}}} = \frac{(a_{\text{SO}_4})^{1/2}}{(a'_{\text{SO}_4})^{1/2}} = \left[\frac{a_{\text{SO}_4}}{a'_{\text{SO}_4}} \right]^{1/2}. \quad (14)$$

Instead of the ionic ratio for sulphate itself being equal to the ionic ratio for hydrogen ion (and hence to the ionic ratios for all univalent ions) we find we must extract the square root of the ratio when the valence is two, and put this square root of the ionic ratio equal to the ionic ratios of univalent ions. When the valence of an ion is n , we must take the n th root. In algebraic language, the quantity $(a'/a)^{1/n}$ has the same value for any ion of valence n , the valence n being considered positive of cations, and negative of anions, so as to invert the ratio in the case of anions.

125. Membrane Potentials.—After the facts cited above were discovered, it was noted that Gibbs, in his monumental paper on the Equilibrium of Heterogeneous Substances,¹ had not only

¹ Published as "Scientific Papers I: Thermodynamics," Longmans, Green & Co., New York, 1906 and 1928. Originally published in 1878.

given all the thermodynamic theory used in the preceding sections, but also an equation [his Eq. (688)] which contains the theory of membrane potentials, although he did not apply it to quite the same case. The mode of thought of Gibbs is very general and powerful, and also very direct, but it is a little difficult for the beginner to grasp. Let us therefore first use the same method we have always used to calculate the electromotive force of a cell. Consider the cell



The broken vertical line indicates a semipermeable membrane, permeable to all the ions but R^- . The two solutions are supposed to be brought to equilibrium with respect to transfer of diffusible ions before the cell is set up, and this type of equilibrium is supposed maintained. Then Eq. (3) will apply, and the ionic ratios for sodium ion and chloride ion will be equal, that is,

$$a'_{\text{Na}}/a_{\text{Na}} = a_{\text{Cl}}/a'_{\text{Cl}}. \quad (16)$$

Suppose one faraday of positive electricity is passed through the cell from left to right, using such large volumes of solution that the concentrations are not appreciably altered. Since the potentials at the junctions indicated by the double vertical bars are supposed eliminated (with salt bridges) we need not consider the free energy changes occurring across these junctions. Similarly, the changes at the two identical but opposed calomel electrodes need not be considered. The free energy changes are due to migration across the membrane, and are occasioned by the transfer of x equivalents of Na^+ from left to right, and of y equivalents of Cl^- from right to left. The fractions x and y are not known, but their sum is evidently unity. Equating the loss of free energy to the electrical work, as in previous chapters, we have

$$E_{\text{F}} = xRT \ln (a'_{\text{Na}}/a_{\text{Na}}) + yRT \ln (a_{\text{Cl}}/a'_{\text{Cl}}). \quad (17)$$

But by Eq. (16) the logarithms must be equal, therefore

$$E_{\text{F}} = (x + y)RT \ln (a'_{\text{Na}}/a_{\text{Na}}) = RT \ln (a'_{\text{Na}}/a_{\text{Na}}) = RT \ln (a_{\text{Cl}}/a'_{\text{Cl}}). \quad (18).$$

By the use of Eq. (18) the electrical potential at the membrane, which is equal to the electromotive force of the cell (15), can

be calculated from the ionic ratio of cations, or of anions, when the valence is unity.

The same method can be extended to a solution in which there is any number of cations and of anions, which may be of any valence, but the following method is simpler and more in the spirit of Gibbs.

The simple method consists in considering only one kind of ion at a time. For example, take again the cell (15) and consider first the sodium ion alone. In justification of this, we note that the membrane actually used would permit all ions to pass except R^- , but if we have equilibrium with this membrane, we should still have equilibrium if this membrane were replaced with one which allows only sodium ions to pass.¹ Hence we may consider the loss of free energy and the electrical work done when one faraday passes through the cell causing migration of sodium ions alone through the membrane. We thus obtain at once

$$E_F = RT \ln (a'_{Na}/a_{Na}). \quad (19)$$

We may treat any other ion separately. In the case of any anion, when the faraday is passed through the cell from left to right, the anion will pass the membrane in the opposite direction, so that we shall have for a chloride ion

$$E_F = RT \ln (a_{Cl}/a'_{Cl}). \quad (20)$$

Notice the inversion of the ionic ratio.

In the case of a cation of valence n_{cat} , since each ion carries only n_{cat} charges of electricity, only $1/n_{cat}$ of a mole of the ion will pass the membrane per faraday. We shall have

$$E_F = (RT/n_{cat}) \ln (a'_{cat}/a_{cat}) = RT \ln (a'_{cat}/a_{cat})^{1/n_{cat}}. \quad (21)$$

For an anion of valence n_{an} we shall have

$$E_F = RT \ln (a_{an}/a'_{an})^{1/n_{an}} = RT \ln (a'_{an}/a_{an})^{-1/n_{an}}. \quad (22)^2$$

Provided, therefore, we think of the valence as an algebraic quantity, positive for cations and negative for anions, we shall have for an ion of valence n

$$E_F = RT \ln (a'/a)^{1/n}. \quad (23)$$

¹ With regard to the legitimacy of assuming the existence of all kinds of semipermeable membranes, see remarks in Chap. VI, page 48.

² From algebra, $x^a = (1/x)^{-a}$.

Furthermore, there is only one electrical potential at the membrane, affecting all the ions. We shall therefore have, for *any* two ions,

$$E_F = E_F = RT \ln (a'/a)^{1/n} = RT \ln (a'/a)^{1/n}. \quad (24)$$

Hence, the ionic ratio, $(a'/a)^{1/n}$, has the same value at equilibrium for every ion (n being taken algebraically).

By means of Eq. (23) we can calculate the electromotive force of the cell (15) if the ionic ratio is known for any ion, and likewise can calculate the ionic ratios for all the ions if the electromotive force is measured.

It is not always easy to measure the concentrations of the ions. Analysis does not give the concentration of the ions actually present, but gives the total amount of chloride or other ion-constituent.¹ But hydrogen ions are always present in aqueous solutions, and the activity of hydrogen ions is usually easily measurable by the use of cells for the determination of pH. In view of the preceding discussion the electromotive force of cell (15) is given by the equation

$$E_F = RT \ln \left(\frac{a'_n}{a_n} \right) = \frac{RT}{0.4343} (\text{pH} - \text{pH}'). \quad (25)$$

All the results of this section are precise in terms of activities, subject to the complete elimination of diffusion potentials as indicated in the cell formula. In view of the importance of the subject and the difficulties of making precise measurements, the results as interpreted in terms of ionic concentrations are useful approximations.

Our equations give the sign of the electromotive force when the cell is arranged as in the cell formula (15), the non-diffusible ion being an anion. If the non-diffusible ion is a cation, the effects will be opposite, and also the electromotive force.

Simple statements are possible which give the direction of the effects and of the electromotive force. Whichever the sign of the non-diffusible ion, the other ions of like sign act as if repelled, and accumulate in greater concentration on the side of the membrane opposite to that of the solution containing the non-diffusible ion, whereas the ions of unlike sign act as

¹ Chap. XIV, p. 119,

if attracted, and they accumulate on the same side. These effects are produced when equilibrium is secured by the use of the semipermeable membrane, no electrical current being allowed to flow.¹

To find the direction of the electromotive force, consider how the cations would move if the terminals of the cell were short-circuited with a wire. In this case the cations would move across the membrane from high concentration to low (or from high activity to low). If this movement is found to occur from left to right, as the cell formula is written, then there is a tendency of positive electricity to move from left to right through the cell, and the electromotive force of the cell as written is positive. If the movement of cations is opposite, the electromotive force is negative. These simple statements are given as helpful rules, not as explanations.

126. The Osmotic Pressure of Congo Red.—The osmotic pressure of a solution containing such a substance as Congo red together with diffusible salts will be the difference, of the pressure on this solution minus the pressure on the other solution (outside the membrane and containing the diffusible salts without the Congo red), when the pressures are so adjusted as to make the vapor pressure of water the same in both solutions. According to the simple theory, the pressure required on a solution of ions to make its vapor pressure the same as that of pure water is RTc , where c is the concentration of ions in moles per liter, and therefore the osmotic pressure π is proportional to the difference of the concentrations of the ions in the two solutions; that is,

$$\pi = RT(c' - c),$$

where c' is the concentration of ions of all kinds inside the membrane and c is the concentration of ions of all kinds outside the membrane, these concentrations being in moles per liter (not necessarily in equivalents per liter).

There is an interesting result of the theory which we shall here state without proof. In general, the osmotic pressure lies

¹ That is, no cell is set up, or if a cell is set up the electrodes are not connected by a wire. When a cell is set up it may be connected to a potentiometer, but when this is properly operated, practically no current is allowed to pass through the cell, so that the equilibrium is not disturbed.

between the osmotic pressure that would be produced by all the ions of Congo red (neglecting all other ions) and the osmotic pressure that would be produced by only the non-diffusible ions of Congo red (neglecting all other ions). The addition of diffusible salts to the system lowers the osmotic pressure, from one extreme towards the other.

127. Interfacial Potentials.—The production of electrical effects in the animal body is but imperfectly understood. The ordinary electrical cells, with electromotive forces of one or two volts, contain metals, and free metals are not found in the animal body. Liquid junction potentials, produced with such aqueous solutions as may be expected to occur in the animal body, amount to only a few millivolts. The Donnan membrane potentials may help in the interpretation of animal electricity. A study which has been carried further in an effort to explain electrical effects of biological origin, especially by Beutner, is that of the potential that may occur at the interface between two partially miscible liquids, such as oil and water. Beutner has been able to set up cells with electromotive forces of the order of one-tenth volt, without the aid of dissimilar metals or of non-diffusible ions. These electromotive forces are believed principally due to the potentials at phase boundaries.

If an electrolyte such as NaCl is dissolved in water and the water solution shaken with a suitable oil until equilibrium is reached, the partial molal free energy of NaCl must be the same in the oily phase as in the watery phase. This does not necessitate that the partial molal free energy of the Na^+ and Cl^- ions should separately be the same in each phase, but only that their sum should be the same. If the partial molal free energy of, say, the sodium ion differs in the two phases at equilibrium, there will be an electric potential at the boundary, since the electrical work $E\mathcal{F}$ done when we pass a faraday across the boundary must be equal to the difference of free energy, and E cannot be zero when the difference of free energy is not zero. In order to show that the difference of free energy is not zero we shall consider that the solutions in both phases are very dilute, so that we may use concentrations rather than activities.

Suppose that the ion Na^+ is perfectly free to distribute itself between the two phases, in a concentration ratio (the distribution

coefficient) dependent on the nature of the phases and of the ion itself. Suppose also that the ion Cl^- is similarly free. Then if it happens that the distribution coefficient is the same for both ions, there will be no conflict of tendencies of the ions to pass from one phase to the other, the partial molal free energy of Na^+ can become the same in both phases at equilibrium (and also that of Cl^-), and the interfacial potential will be zero. With a suitably chosen oil, this might of course happen. But with one kind of oil, it could not happen for all salts.

For, suppose it could in fact happen for NaCl , for KCl , and for other salts. Then the distribution coefficient must be the same for Na^+ , Cl^- , and for K^+ , and indeed for all the ions concerned. But the distribution coefficient for Na^+ and for Cl^- is the distribution coefficient for the salt NaCl itself, as in the very dilute solutions the ionization is supposed complete, so that the concentration of Cl^- ions in either phase equals the concentration of NaCl . Similarly for the other salts. Thus if the distribution coefficient is the same for all the ions, the distribution coefficients of all the salts must be the same for a given oil, and this is known not to be the fact.

Thus we conclude that the distribution coefficients of the cation and anion of a given salt are not in general equal. If the distribution coefficient of the cation in favor of the oil¹ is greater than that of the anion its movement towards the oil will be hindered by the anion, as there must not be any appreciable excess of cations over anions in the oil, but both solutions must be practically neutral. There will be produced only that very slight excess of cations in the oil, and equal deficit of cations in the water, necessary to produce a potential at the boundary. If the two phases are incorporated into a cell, and the electrical circuit is completed so that current may flow, the cations in this case will move across the boundary into the oil, and the anions into the water, that is, the potential at the boundary, water | oil, will be positive as written.

An expression for the potential E of the boundary

$$\text{NaCl in water,} \quad \left| \quad \text{NaCl in oil,} \right.$$

$$a'_{\text{Na}}, a'_{\text{Cl}} \quad \left| \quad a''_{\text{Na}}, a''_{\text{Cl}} \right.$$

¹ The distribution coefficient *in favor of the oil* is simply the concentration in oil divided by the concentration in water, at equilibrium.

may be found by supposing one faraday to pass across the boundary from left to right, and the Na^+ ions alone to move. Then the loss of free energy is $RT \ln a'_{\text{Na}} + k'_{\text{Na}} - RT \ln a''_{\text{Na}} - k_{\text{Na}}''$. We have then

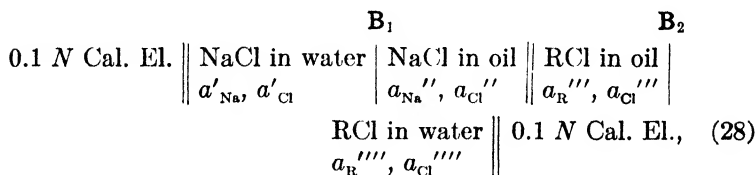
$$E_F = RT \ln (a'/a'')_{\text{Na}} + (k' - k'')_{\text{Na}}. \quad (26)$$

Similarly, by supposing only Cl^- ions move (from right to left) when the faraday is passed, we obtain the equation

$$E_F = RT \ln (a''/a')_{\text{Cl}} + (k'' - k')_{\text{Cl}}. \quad (27)$$

This case is sharply distinguished from the Donnan equilibrium, where the constants in the free energy expressions could be canceled. Equations (26) and (27) cannot at present be used to calculate the value of the potential from the activities or concentrations, as the k constants are not usually known. Also, it is not known how to arrange a cell in which a single boundary potential like that above shall be the only potential.

By arranging two boundary potentials in opposition, we can eliminate some of the unknown constants. Consider the combination



where the same oil is used on both sides of the cell, but RCl , a strongly ionized chloride other than sodium chloride, is used on the right. The water and oil phases separated by the boundary B_1 are supposed to be brought to equilibrium with respect to transfer of sodium chloride before the cell is set up, and likewise the two phases separated by the boundary B_2 are supposed in equilibrium with respect to transfer of RCl . Let us suppose that we can connect the two oil phases with each other, and the two water phases each with a calomel electrode, with the elimination of liquid junction potentials, as indicated by the double vertical bars. Then when a little current is supposed passed through the cell there will be no free energy changes to consider except those at the boundaries B_1 and B_2 , as all other free energy

changes are either zero or canceled. The chloride ion is common to all four phases concerned in the boundaries, and it is convenient to suppose that one faraday is passed from left to right through the cell, carrying only chloride ion across the boundaries (from right to left). We shall have

$$E_F = RT \ln (a''/a')_{\text{Cl}} + (k'' - k')_{\text{Cl}} + RT \ln (a'''/a'')_{\text{Cl}} + (k'''' - k''')_{\text{Cl}}. \quad (29)$$

But k_{Cl}'''' is for Cl^- in water, and is the same as k'_{Cl} ; and likewise, k_{Cl}''' is for Cl^- in oil and is the same as k''_{Cl} . Hence all the k constants may be canceled.

If our solutions are not too strong we may use concentrations instead of activities in Eq. (29). Then we shall have

$$E_F = RT (\ln c'' - \ln c' + \ln c'''' - \ln c''')_{\text{Cl}}. \quad (30)$$

If we now arrange the experiment so as to have the concentrations of chloride the same in the two water phases $c'_{\text{Cl}} = c_{\text{Cl}}''''$ we shall have simply

$$E_F = RT (\ln c'' - \ln c''')_{\text{Cl}} = RT \ln (c''/c''')_{\text{Cl}}. \quad (31)$$

Beutner set up various cells of this type. Using guaicol as oil and dimethylaniline hydrochloride as RCl , the measured electromotive force was -0.091 volt, when the calculated value was -0.1 volt. In practice, no special means was used to eliminate the liquid junction potential between the two oil phases. It is believed to be very small.¹ The agreement obtained between observed and calculated values of the electromotive force was in general very good, considering the approximations made.

When the total electromotive force is 0.1 volt, it does not mean that the two boundary potentials are each less than 0.1 volt. On the contrary, they are very likely greater, as we should expect to measure the difference, rather than the sum, of the two boundary potentials when the two boundaries have their water and oil phases arranged oppositely, as in the case of the cell (28).

¹ The magnitude of liquid junction potentials depends greatly on the difference of the mobilities of anion and cation, and the difference is usually smaller in non-aqueous solutions than in aqueous solutions.

A simple rule can be given for the direction of the electromotive force in cells such as (28), provided the concentration of the common ion is the same in the two water phases. The common ion has a tendency to pass from the oil phase in which it is stronger into the other oil phase, but a consideration of this tendency cannot explain the electromotive force, as the liquid junction potential between the oils is negligible.¹ However, the tendency of the common ion to pass from oil to water is greater in the case of the oil phase in which the common ion is stronger, because the two water phases are of equal strength in the common ion. When the circuit is completed electrically the common ion can pass in only one direction through the cell, and it will pass from that oil phase in which it is stronger into the neighboring water phase. If this motion is the same as would be produced by passing positive electricity through the cell from left to right, the electromotive force and likewise the pole sign of the electrode on the right of the cell are positive, and otherwise, the sign is negative.

Instead of preparing two separate oil phases, each saturated with its water phase, one oil phase may be interposed between the two water phases. On standing, the layers of oil next the water phases come to equilibrium with the adjacent water layers, thus establishing the phase boundary potentials. Beutner set up cells of this and of other types. In any case, the electrical energy which can be delivered in the operation of such cells is very small, and a quadrant electrometer instead of a galvanometer is generally used in the electromotive force measurements.

For further information on this subject the reader is referred to Michaelis'² "Hydrogen Ion Concentration."

¹ If we consider this tendency, and this tendency alone, we shall arrive at exactly the wrong answer in the present case.

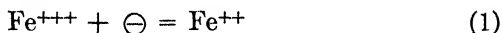
² In his discussion of Beutner's cells, the sign of the cell discussed in the text above is incorrectly given on page 193. The sign is given by Beutner in his general discussion of these cells and the interpretation of bioelectric phenomena in "Die Entstehung Elektrischer Ströme in Lebenden Geweben." (Inaugural Dissertation of Reinhard Beutner, Friedrich-Wilhelms-Universität.) Ferdinand Enke, Stuttgart, 1920.

CHAPTER XXVI

OXIDATION AND REDUCTION POTENTIALS

In the last few years the study of oxidation and reduction in biological systems has been greatly furthered by the application of measurements of the electromotive force of cells. These cells consist of a reference electrode and a half cell made up of a plate of platinum or other inert metal immersed in the solution to be studied; the two half cells being connected by a salt bridge.

128. Conditions for a Stable Electromotive Force.—If ferric ions are present in the solution, then on passing current in the proper direction they can be reduced with the aid of electrons from the metal; if ferrous ions are present, they can undergo oxidation with the liberation of electrons to the metal; and when both are present in sufficient quantities, electrons can pass from or to the metal, being absorbed or produced by the solution by means of the electrochemical reaction

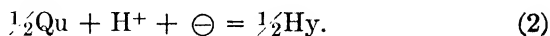


and its reverse. Under these conditions the electromotive force of the cell can be measured experimentally.

In order to have a stable electromotive force when the half cell is combined with a good calomel or hydrogen electrode, it is necessary that in the half cell there be present in reasonable quantities all the substances involved in some electrochemical process, and that this process occur with a reasonable velocity. If they are not present, the cell may have a potential, but we cannot measure it, as the passage of ever so little current in one direction or the other will produce sufficient change of composition in the immediate neighborhood of the inert metal to affect the potential to a great extent. Such an effect is called polarization.

Ferric and ferrous ions may be regarded as two forms of iron. Ferric ion, being in the more highly oxidized state, we shall call

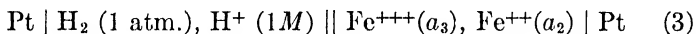
the oxidant; and ferrous ion, the reductant. Quinone (Qu) is another example of an oxidant, hydroquinone (Hy) being the corresponding reductant. In this case the hydrogen ion is involved in the electrode process



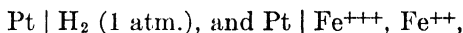
The reason for not mentioning the hydrogen ion as an oxidant—and it really is one, equally with the quinone—is simply that hydrogen ions are present in every aqueous solution and do not always require mention.

For a stable electromotive force, both oxidant and reductant must be present in appreciable quantities in the half cells, and the electrochemical process must be one that can take place with a reasonable velocity.

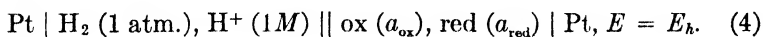
129. The Oxidation Potential.—When we have a cell such as



the total electromotive force E will be the difference of the single electrode potentials when both are written with the metal at the left, as



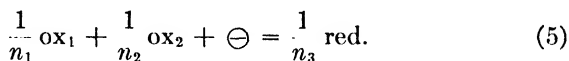
or will be the sum of the single potential of the hydrogen electrode plus the potential of the ferric-ferrous electrode when this is written with the metal at the right, as in cell (3). We shall call the potential of the ferric-ferrous electrode, or of any oxidant-reductant electrode, the *oxidation potential* E_h of the ferric-ferrous solution or other solution, when the formula for the half cell is written with the metal at the *right*, as in the cell (3), the potential of the molal hydrogen electrode being put equal to zero as usual:



We abbreviate oxidant to "ox" and reductant to "red."

Thus the oxidation potential E_h is here defined with the elements of the half cell in the opposite order to that previously used for single electrode potentials, and the algebraic sign is accordingly opposite. This makes our E_h the same as that of Clark.

We can derive the equation for the electromotive force of a cell such as (4) if we know the equation for the electrochemical process. This equation is to be written as a cathodic process, and for one faraday. The form of the equation depends on the nature of the process. One form, quite commonly occurring, is



Here, $1/n_1$ and $1/n_2$ are the numbers of moles of oxidants disappearing per faraday, and $1/n_3$ is the number of moles of reductant formed. An example is Eq. (1), in which case ox_1 is Fe^{+++} , red is Fe^{++} , and $1/n_1$ and $1/n_3$ are each unity, $1/n_2$ being zero. Another example is Eq. (2). Here ox_1 is quinone, ox_2 is the hydrogen ion, and red is hydroquinone; $1/n_1$ and $1/n_3$ are each equal to $1/2$, and $1/n_2$ is unity.

Since the partial molal free energy of any of the oxidants or reductants is given by an expression of the form $RT \ln a + k$, the loss of free energy attending the electrochemical process (5) is

$$(1/n_1)[RT \ln (\text{ox}_1) + k_1] + (1/n_2)[RT \ln (\text{ox}_2) + k_2] - (1/n_3)[RT \ln (\text{red}) + k_3].$$

When one faraday is passed from left to right through the cell (4) without appreciably affecting the concentrations, the electrical work E_F equals the loss of free energy occurring in the cell, and hence equals the loss of free energy attending the cathode reaction, as the free energy change at the molal hydrogen electrode is put equal to zero, like its potential. Equating the electrical work to the loss of free energy and combining logarithms and constants,

$$E_F = E_{hF} = RT \ln \frac{(\text{ox}_1)^{1/n_1} (\text{ox}_2)^{1/n_2}}{(\text{red})^{1/n_3}} + \text{a constant.} \quad (6)$$

This equation is exact if we understand the parentheses to indicate activities, and will be in most cases exact enough if we take them to indicate concentrations.

When the activities of all oxidants and reductants are unity, the logarithmic term is zero. Calling the value of the electro-

motive force E_0 when this is the case, we see that the value of the constant of Eq. (6) is E_0F .

$$E_{hF} = E_0F + RT \ln \frac{(\text{ox}_1)^{1/n_1}(\text{ox}_2)^{1/n_2}}{(\text{red})^{1/n_3}} \quad (7)$$

Applying now the conventional rule for writing mass action functions to the electrochemical process (5) we have for the value of this function K ,

$$\ln K = \ln \frac{(\text{red})^{1/n_3}}{(\text{ox}_1)^{1/n_1}(\text{ox}_2)^{1/n_2}} = -\ln \frac{(\text{ox}_1)^{1/n_1}(\text{ox}_2)^{1/n_2}}{(\text{red})^{1/n_3}} \quad (8)$$

The value of the oxidation potential of a cell such as (4) is therefore given by the expression

$$E_{hF} = E_0F - RT \ln K. \quad (9)$$

This expression holds for even more complicated electrochemical reactions, provided only that the mass action function K is written for a cathodic reaction and for one faraday. Notice that the activities or concentrations used in the function K are those for the concentrations obtaining in the half cell as the cell is set up, and are not the activities that would obtain if the whole cell were short-circuited, thus bringing about a chemical equilibrium. Thus K is the same as K' of Eq. (22) of Chap. XX (page 183).

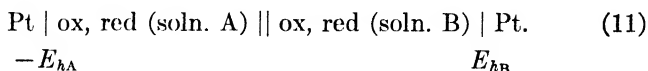
When there is only one oxidant and one reductant, the same number of moles $1/n$ of each being involved in the electrochemical equation, simplification is possible, and we can easily obtain an equation given by Clark

$$E_h = E_0 - \frac{RT}{nF} \ln \frac{(\text{red})}{(\text{ox})} \quad (10)$$

as the general form of the Peters equation. Many books have given similar equations and have called n the valence. The practice of regarding n as the valence has proved to be very confusing to students, who cannot answer the question, "Valence of what?" The quantity n has of course to do with a change of valence, but it is clearer to explain the occurrence of n in the formula by saying that $1/n$ is the number of moles of oxidant reduced to $1/n$ moles of reductant by one faraday. In the

general equation (9) no n occurs, but certain powers will occur in the equilibrium function.

130. The Level of Oxidation or Reduction.—Suppose we set up a cell as follows:

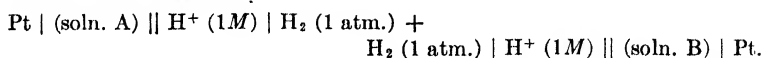


The electromotive force of this cell will be $E_{hB} - E_{hA}$, as the half cell B is written in the conventional manner for an oxidation potential, and the half cell A in the opposite manner.¹ If this potential difference is positive, E_{hB} being more positive than E_{hA} , there is, according to our unvaried convention, a tendency of positive electricity to pass through the cell from left to right. When the electrical circuit is completed, the cathode will be at the right and the solution B will be reduced. In the operation of the cell, the oxidant of solution B oxidizes the reductant of solution A. We shall say that solution B is in such a case more oxidizing, or is at a higher level of oxidation, than solution A. The greater the oxidation potential of a solution, the greater is the tendency for it to oxidize the reductant of another given solution when the two solutions are placed in a cell with elimination of liquid junction potential. We have chosen to call E_h definitely the *oxidation* potential to emphasize that the level of oxidation is greater, the greater this potential is algebraically.

As is shown by our electromotive force equations, especially Eq. (6), the oxidation potential and the level of oxidation are greater, the greater the activity of oxidant relatively to the activity of the reductant in the solution. In dilute solutions this will also be true with respect to the relative concentrations of the oxidant and reductant.

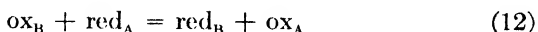
If the solutions A and B should be mixed, there is a probability that the same oxidation-reduction process will occur as takes

¹ Following the method explained in Chap. XVIII we can show this from the consideration that E is equal to the sum of the electromotive forces of the two cells in series:



The potentials of the molal electrode would cancel, even if not put equal to zero by our convention.

place when the cell operates, and indeed as a chemical, rather than as an electrochemical, reaction. This is evident from the consideration that the electromotive force of the cell is due entirely to the tendency for the two electrochemical reactions, which sum up to one chemical reaction, to take place. This chemical reaction may be represented by an equation such as



to take a simple case, and considering E_{hB} greater than E_{hA} . Considered as a purely chemical reaction, the tendency of it to take place is diminished by the presence of the products, red_B and ox_A , according to the mass action principle. This is consistent with the effect of the reductant of solution B in diminishing its oxidation potential, and with the effect of the oxidant of solution A in increasing its oxidation potential.

Chemical actions other than those possible during cell operation may occur in some cases when solutions are mixed. A matter of especial importance is the hydrogen-ion concentration. The pH may be different for the two solutions, as placed in the cell, but must have only one value, in general different, for the mixture. When the electrochemical process involves the hydrogen ion, the value of E_h depends on the hydrogen-ion activity. For this reason alone, we cannot in all cases predict, from a simple knowledge of the two oxidation potentials, what would happen if two solutions are mixed.

131. Indicators of Oxidation and Reduction.—Many highly colored dyestuffs can be reduced in the laboratory to colorless substances, which in turn can be oxidized back to the original dyestuffs. Ehrlich found that certain of these were also reduced when injected into the animal body, and to a different extent in the different tissues. This suggested the great importance of the level of oxidation in biological systems, and the usefulness of the oxidation potential as a measure of the level of oxidation. W. Mansfield Clark has found it possible to use certain dyestuffs as indicators for the measurement of oxidation potential.

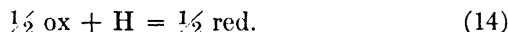
The highly colored substance may be added in very small quantity to a solution to be tested. Thus it has but a small effect on the oxidation potential and pH of the original solution. When the indicator is a good one (and Clark has found some),

the solution quickly acquires a color depending on the oxidation potential and the pH, the indicator being partly oxidized or reduced by the constituents of the solution and coming to chemical equilibrium with them.

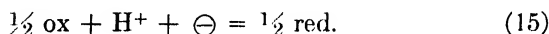
In order to see how the E_h can be computed from the measurement of color and the pH, let us imagine that a cell is set up with the solution plus indicator at the right:



Let the concentrations of the two forms of the oxidation indicator be denoted by (ox) and (red), respectively. Let the oxidation indicator be such as can be reduced by an atom of hydrogen according to the chemical equation



Then this might happen electrochemically at a cathode, according to the equation



By considering one faraday to pass through the cell, and this process (15) to occur alone, without the other possible electrode processes, we obtain the equation

$$E_h = E_0 - \frac{RT}{F} \ln \frac{(\text{red})^{\frac{1}{2}}}{(\text{ox})^{\frac{1}{2}}(\text{H}^+)}, \quad (16)$$

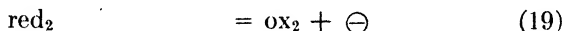
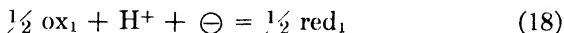
which can be simplified to

$$E_h = E_0 - \frac{RT}{0.4343F} \text{pH} - \frac{RT}{2 \times 0.4343F} \log \frac{(\text{red})}{(\text{ox})}. \quad (17)$$

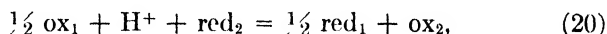
There will be, besides the above equation for the indicator forms, a separate equation for each substance present in two forms (oxidant and reductant) in the solution, each equation having the same E_h . This is true, provided simply that all these substances come to equilibrium with one another with respect to the oxidations and reductions in question. It is quite enough, if only one pair of forms come into equilibrium with the platinum with respect to the electrochemical process. This is in consequence of the principle that on passing a small amount of current the loss of free energy must be the same for one electrode process

as for any other when all the substances involved in the electrode processes are in chemical equilibrium.

For suppose the loss of free energy were greater for one of these processes—say, $\frac{1}{2} \text{ox}_1 + \text{H}^+ + \ominus = \frac{1}{2} \text{red}_1$ —than for another—say, $\text{ox}_2 + \ominus = \text{red}_2$ —then the two processes



sum up to a chemical reaction,



that could occur with a loss of free energy, contrary to the assumption of chemical equilibrium among the substances. Thus the derivation of Eq. (17) does not require that the electrochemical process (15) be possible for the indicator.

Experimentally, we can determine the concentration ratio (red)/(ox) of the indicator in a solution by comparison of the color of the unknown with the color seen when the indicator is distributed between two tubes in various ratios—the indicator in one tube being oxidized, and that in the other, reduced—and the light passes through the two tubes in succession before reaching the eye. Thus the ratio (red)/(ox) is determined optically, and E_h is calculated by means of an equation from this ratio and the value of the pH.

Clark found several indicators to which Eq. (17) might be applied, when the solution is a little acid. But in neutral and alkaline solution, the hydrogen ion appears to act in more than one way, and E_0 of Eq. (17) is not truly constant when the pH is varied too much, though it remains constant for variations of the ratio at constant pH. Clark accordingly writes the equation

$$E_h = E_0' - \frac{RT}{2F} \ln \frac{(\text{red})}{(\text{ox})}, \quad (21)$$

where the parentheses indicate concentrations, and gives values of E_0' for various values of the pH.¹

¹ "The Determination of Hydrogen Ions," 3d ed., Table L, Appendix, p. 683.

132. The Effect of pH on the Oxidation Potential E_h .—When the electrochemical process does not involve the hydrogen (or hydroxyl) ion, and likewise the chemical reaction, oxidant to reductant, does not involve hydrogen (or oxygen), then the oxidation potential will depend only on the activities of the oxidant and reductant and not upon the activity of hydrogen ion. When the hydrogen ion is involved, it always acts as an oxidant to increase the oxidation potential. Hence, any solution is likely to be less oxidizing at higher pH values.

It is clear that measurements of oxidation potential should in any case be accompanied by measurements of pH.

133. The Use of Calomel Electrodes.—Although the molal hydrogen electrode is used for the definition of E_h , it is more convenient in actual measurements to use a calomel electrode. The computation involves nothing new for those who have read previous chapters. The result is

$$E_h = E + k, \quad (22)$$

where E is the electromotive force of the cell



and k is the value for the particular calomel electrode, as given by Clark,¹ who gives potentials for electrodes as written in the order: soln., metal. Thus, for the saturated KCl calomel electrode, k at 25° is given as +0.2458 volt.

In experimentation with cells for the determination of pH, the wire from the calomel electrode is always to be connected with the "plus e.m.f. terminal" of the potentiometer. But this will not always be the case when measurements of oxidation potential are being made. If, when cell (23) is studied, it is found necessary to connect the platinum plate of the oxidation half cell to the plus e.m.f. terminal of the potentiometer in order to obtain a balance, then the value of E in Eq. (22) is positive; otherwise, negative.

134. Application and Difficulties.—In the formulas for oxidation potential the absolute concentrations of oxidant and reduc-

¹ *Ibid.*, Table A, p. 672.

tant do not matter but only their ratio.¹ We may have then a given high level of oxidation produced by a large amount of material, or by a small amount. In some biological systems the amount of material responsible for the oxidation potential may be of great importance; for instance, bacteria may in their metabolism use up oxidants and thus greatly change the oxidation potential of the medium, if this is the result of small amounts of material. The oxidation potential does not measure the amount of oxidizing or reducing substance, but only the level of oxidation as defined above.

The difference in pH between a normal solution of hydrogen ions and a normal solution of hydroxyl ions corresponds to about 0.8 volt. Due largely to the efforts of men still living, this interval has been subdivided into very small intervals of importance, 0.02 volt being now regarded as a rather gross interval (about 0.3 pH). From a solution saturated with oxygen at 1 atm. to a solution of the same pH, but saturated with hydrogen at 1 atm., there is a decrease of oxidation potential of about 1.227 volts at 25°. ² From research now being actively prosecuted in various laboratories it appears that the subdivision of this interval is of equally great importance.

The investigator in pure physical chemistry has never been interested in measurements of electromotive force unless he has known the electrode processes. The biologist also seeks to learn what are the electrode processes back of an oxidation potential, but can afford to attempt to correlate biological phenomena with oxidation potentials even if without hope of discovering the nature of the electrode processes.

A prime difficulty is that many substances of known ability to oxidize (or reduce) do not enter into an electrode process, at least with sufficient speed to be effective. They are "electromotively inactive." Thus the oxidation potential may not

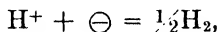
¹ This is according to the simple theory, in which concentrations are used in place of activities, but in any case holds only when the number of moles of reductant in the electrochemical equation is the same as the number of moles of oxidant.

² This difference is the calculated value of the electromotive force of the "Knallgas" cell and is almost independent of the pH; indeed, any variations depend on the small variations of the activity of the water in the solutions.

take into account some of the most important substances. Yet it is sometimes possible to add a substance capable both of entering into an electrochemical process and of coming to chemical equilibrium with the important substances. Such a substance is said to transfer the potential of the electromotively inactive substances to the electrode.

Another difficulty of interpretation is due to the fact that the oxygen of the air is electromotively active. It does not enter into a unique electrode process (this would make the oxygen electrode useful for measuring the hydroxyl-ion concentration), but it enters into some electrode process fast enough to interfere with the measurement of some oxidation potentials. A simple remedy, in principle, is to work in the absence of oxygen. But this has to be applied with great caution, if the normal state of the biological system to be studied depends on the presence of air.

When an acid-base system has a pH definitely supported by substantial quantities of acid and basic substance, it is said to be well buffered. When an oxidation-reduction system has an oxidation potential well supported by substantial quantities of oxidant and reductant, by means of a rapid electrode process, it is said to be well poised. Now, the pH of well-poised systems can rarely be measured by means of the hydrogen electrode, as this would ordinarily reduce the oxidant, violating the condition essential for the electrometric measurement: that the process,



be the unique process at the hydrogen electrode. The quinhydrone electrode may also fail. The glass electrode is usually applicable, except in too alkaline a solution. Thus, we shall often have to depend on the indicator method of determining pH.

The reader is referred for further information to Clark's "Determination of Hydrogen Ions,"¹ and particularly to the more recent "Oxidation-reduction Potentials,"² by Michaelis.

¹ Third edition, The Williams and Wilkins Company, Baltimore, 1928.

² Translated by Flexner, J. B. Lippincott Company, Philadelphia, 1930.

CHAPTER XXVII

THE HEAT OF REACTION AND THE EFFECT OF TEMPERATURE AND PRESSURE ON CHEMICAL EQUILIBRIUM

If water and sulphuric acid at the same temperature, say that of the room, are brought together and mixed, the temperature of the fluid increases and heat passes from the fluid to the room. A reaction has taken place. The quantity of heat, the removal of which is exactly sufficient to bring the mixture and its container back to the initial temperature, is called the heat of the reaction at this temperature. The qualifying phrase "at this temperature" is necessary, as the heat of reaction is generally different at different temperatures. The phrase implies that the same heat might be removed, but in such a way as to keep the temperature always the same, and this can be proved from the first law of thermodynamics to be true, provided the pressure is kept constant during the whole process, or else the substances are kept throughout the process in a container of constant volume.

When the temperature tends to rise during a chemical reaction, so that heat must flow *out* if we are to keep the temperature constant, the reaction is called *exothermic*. If the temperature tends to decrease, so that heat must flow *in* to keep the temperature constant, the reaction is called *endothermic*.

The measurement of the heat flow will be briefly discussed in a later section.

135. The Energy and Heats at Constant Volume.—The energy of a system represents the combined capacity of the system for doing work and giving out heat. When the system is kept in a container of constant volume, no work is done when the reaction takes place, so that the heat given out is exactly at the expense of the energy of the system. If indeed, we write E_{rea} for the energy of the reacting substances (the reactants) at the temperature T , and E_{pro} for the energy of the products

at the same temperature, then the heat of reaction at T° is equal to $E_{\text{rea}} - E_{\text{pro}}$. The heat of reaction is regarded as positive when heat is given out to the surroundings; negative, when the system absorbs heat.

The energy, either of reactants or of products, depends only on the state of the system, so that $E_{\text{rea}} - E_{\text{pro}}$ depends only on the *change of state*. Hence, at constant volume, the heat of reaction also depends only on the change of state, and is the same, whether heat is withdrawn (or added) at exactly the rate necessary to keep the temperature constant, or whether the temperature rises (or falls) adiabatically (that is, without addition or withdrawal of heat) to its fullest extent and then the necessary heat is transferred to restore the initial temperature.

The energy of a gram of a substance of given composition depends on the temperature and slightly upon the pressure. The energy is an additive property, that is to say: (1) the energy of a system is equal to the sum of the energies of its parts, (2) the energy of x grams of a substance of given composition is exactly x times the energy of one gram at the same temperature and pressure,¹ and (3) the energy of zero grams of a substance is zero.

At constant temperature, the change of energy with the pressure is usually very small in comparison with the energy changes due to chemical reactions. The energy of a substance increases with the temperature, and the rate of increase per unit temperature increase at constant volume, which is denoted in the calculus by $(dE/dT)_v$, is equal to the heat absorbed per unit temperature increase at constant volume, which is called the heat capacity of the substance at constant volume. The heat capacity is also an additive property in the sense defined above. The heat capacity of one gram is called the specific heat; that of one mole is called sometimes the molal heat capacity, sometimes the specific heat per mole. The word *specific* signifies a reference to some unit of quantity of substance, such as gram or mole; it no longer refers to a comparison with water.²

¹ Strictly speaking, in the same state. For chemical purposes the state is sufficiently specified when we give the composition, pressure, and temperature.

² The idea of the calorie involves the use of water as a reference substance. But in the modern measurement of heat capacity one determines, not the

In the bomb calorimeter, chemical reactions are carried out at practically constant volume, and therefore, as explained above, the measurement of the heat of reaction gives directly the energy loss due to the reaction. The change of state will be of the type

Reactants at T_1, p_1 = products at T_1, p_2 (constant volume). (1)

A change of state more convenient to discuss is

Reactants at T_1, p_1 = products at T_1, p_1 (constant pressure). (2)

Now, the energy change for the hypothetical change of state

Products at T_1, p_2 = products at T_1, p_1 , (3)

may ordinarily be regarded as zero, since the energy depends but little on the pressure at constant temperature. Hence the energy change for reaction (2) may be taken as the same as for reaction (1) as studied in the bomb calorimeter. For, the change of state (2) will be attended by the same *energy change*, whether it is brought about in one direct process (2), or in two steps (1) and (3), since the energy is determined by the state. On the other hand, the heats of the two reactions (1) and (2) are not the same, as will appear below.

136. The Heat Content and Heats at Constant Pressure.---

The "heat content" is simply the name for a sum $E + pV$, the energy of a system plus the product of its pressure times its volume. It is assumed that pV will be expressed in the same energy units as E in any numerical calculations. We do not of course know the absolute value of the energy, and therefore not that of the heat content; we deal exclusively with differences of energy and differences of heat content. The symbol Δ (delta) is generally used for differences, when they are not infinitesimally small. If the energy is changed from E_1 to E_2 , we write ΔE for $E_2 - E_1$, that is, Δ stands for an increase, though this may of course be negative, as when E_1 exceeds E_2 .

quantity of heat necessary to raise the temperature, but the quantity of electrical energy dissipated in a resistance wire in contact with the substance. Thus the calorie is not used at all. The specific heats are often reported in joules per degree and per gram, but are usually also computed in some kind of calorie (usually the 15°-gram-calorie), by the use of a conventional value of the mechanical equivalent of heat.

The heat content is usually denoted by H . We have then

$$H = E + pV \quad (4)$$

and

$$\Delta H = \Delta E + \Delta(pV), \quad (5)$$

where $\Delta(pV) = p_2V_2 - p_1V_1$. We may not treat Δ as a differential sign, as applied to a product of two or more variables, and put

$$\Delta(pV) = p\Delta V + V\Delta p.$$

This is incorrect when the differences are not infinitesimals, unless either ΔV or Δp is zero.

The heat content of a gram of a substance of given composition depends on the temperature and slightly upon the pressure. The heat content is an additive property, in the sense explained for the energy.

The importance of the heat content to chemists is due principally to two facts:

1. Since the pV product is determined by the state, the heat content is determined by the state, like the energy, and ΔH is independent of the process by which the change is carried out.

2. In a constant pressure process, the loss of heat content equals the heat evolved. This applies to chemical reactions or to any changes of state in which the only work done is that against the external pressure. When the volume expands from V_1 to V_2 against the constant pressure p_1 , the work done is

$$p_1(V_2 - V_1)^1 = p_1V_2 - p_1V_1 = \Delta(pV).$$

If the heat evolved be designated by q , we have therefore for a constant pressure process in which the only work done is work of expansion

$$-\Delta E = q + \Delta(pV)$$

or,

$$q = -\Delta E - \Delta(pV). \quad (6)$$

¹ This is proved in physics. It is easily seen, if the expansion is supposed to take place in a cylinder of cross-sectional area A , provided with a piston. Then p_1A is the force against the piston, and $(V_2 - V_1)/A$ is the distance over which the piston moves. The work done equals the force times the distance. In chemical calorimetry there is no piston, but when gases enter or leave the apparatus at atmospheric pressure work is done by or against the atmosphere. In such an event the gases must enter or leave at the temperature of the reaction, or corrections must be applied.

As $-\Delta H$ also is equal to $-\Delta E - \Delta(pV)$, by Eq. (5), the heat evolved in the constant pressure process equals $-\Delta H$, the loss of heat content.

This is why H is properly named, in full, the "heat function for constant pressure." Other names are "heat function," "total heat," and "enthalpy." The heat function for constant volume is of course the energy itself.

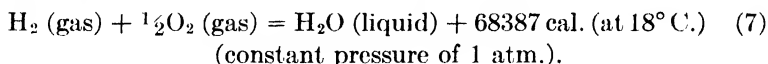
Provided that all processes are carried out at the same constant pressure, the heat evolved in a reaction is determined by the initial and final states, since this is true in any case of its equal $-\Delta H$. Hence, when a chemical change of state is carried out by means of a series of successive reactions, each with its own heat of reaction (the pressure being throughout the same and constant), the algebraic sum of these heats of reaction equals the heat of reaction for the net change of state, when this is carried out in a direct one-stage process at constant pressure. This is the basis of the use of thermochemical equations.

At constant temperature, the change of heat content with the pressure is usually very small in comparison with the changes of heat content due to chemical reactions. The heat content of a substance increases with the temperature, and the rate of change of heat content per unit temperature increase at constant pressure, denoted by $(dH/dT)_p$, is equal to the heat added at constant pressure per unit increase of temperature, which is called the heat capacity at constant pressure. The heat capacity at constant pressure is also an additive property, and the value for one gram is called the specific heat at constant pressure.

The work of expansion in the constant pressure process sometimes has to be calculated. Only the change of volume due to the production or destruction of gas needs to be considered, as the work corresponding to the change of volume due to changes in the nature of the solids or liquids is usually very small in comparison with the total energy change due to the reaction. The simple gas theory is used. For every mole of gas produced in the reaction at the temperature T and the pressure p , the volume is increased by RT/p . The work done is pRT/p or RT per mole of gas formed. Let Δn be the algebraic increase in the number of moles as the result of the chemical reaction. Then the work done by the system in this reaction is $p\Delta V$ and is equal

to $RT\Delta n$. The gas constant R may be taken as 8.315 joules per mole and per degree Centigrade absolute, or as 1.9869 15°-gram-calories per mole and per degree Centigrade absolute, according as the unit used for the heat is the joule, or the caloric.

137. Thermochemical Equations.—These are usually written for constant pressure reactions. An example is



The quantity +68,387 cal. gives the heat evolved, that is, $-\Delta H$.

For the sake of illustrating the principle, let us calculate the energy loss, $-\Delta E$, for the reaction (7). We note that

$$\begin{aligned}\Delta E &= \Delta H - p\Delta V, \\ -p\Delta V &= -RT\Delta n,\end{aligned}$$

and

$$\Delta n = -1.5 \text{ mols.}$$

At the Centigrade temperature 18° ,

$$\begin{aligned}T &= 291.13, \\ RT &= 578.4 \text{ cal. per mole,}\end{aligned}$$

and

$$-RT\Delta n = +868 \text{ cal.}$$

Hence,

$$\Delta E = -68387 + 868,$$

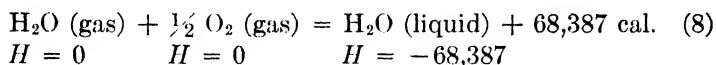
or the loss of energy is 67,519 cal. This is practically equal to the heat of reaction that would be measured in a bomb calorimeter at constant volume. Strictly speaking, the change of state taking place in the bomb calorimeter would be different, as the final pressure would not be the same as in the constant pressure process though both processes start at 1 atm., but the energy depends so little on the pressure that this difference is of small account.

By reversing the calculation, values of $-\Delta H$ for constant pressure processes are often calculated from heats measured in a bomb calorimeter.

The advantage of thermochemical equations is that they may be treated as simultaneous equations. Addition and

subtraction of the equations, including of course the numbers of calories as well as the chemical symbols, is freely permitted, as well as multiplication of all the terms of any equation by a number. Ordinarily one will deal with equations, all of which refer to the same temperature and to the same constant pressure, yet this restriction may be dropped if the numbers of calories refer to $-\Delta H$ rather than to the heat in those cases where the pressure is not constant, and if we are careful to distinguish such quantities as H_2O (liquid, 18° , 1 atm.), H_2O (liquid, 30° , 1 atm.) so as to avoid canceling unlike quantities.

It is often possible in this way to calculate a heat of reaction which has not been measured. There is a system for this. We choose a standard temperature and pressure and choose a standard state for the elements at this temperature and pressure. In general, the state chosen as standard for the element will be the state in which it is usually found at 1 atm. and the standard temperature. Then we put the heat content of all elements in their standard state equal to zero.¹ Applying this convention to Eq. (7) we write



the standard temperature being $18^\circ\text{C}.$, and the standard pressure 1 atm. The quantity $+68,387$ cal. is called the heat of formation of liquid water from the elements. Since this heat of formation represents a loss of heat content and the heat content of the reactants is taken as zero, the liquid water must have a negative heat content,

$$H = -68,387 \text{ cal.}$$

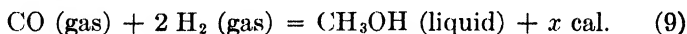
In general, the heat content of a substance is equal to its heat of formation, with the sign changed. Hence, from heats of formation, as found in tables, we can readily find the heat of a reaction: take the heats of formation for all the substances involved in the reaction, change the signs to obtain their heat contents, and compute by how much the heat content of the products is less than that of the reactants. This gives $-\Delta H$, the heat of reaction.

¹ There is no harm in this, since in chemical reactions one element is never converted into another,

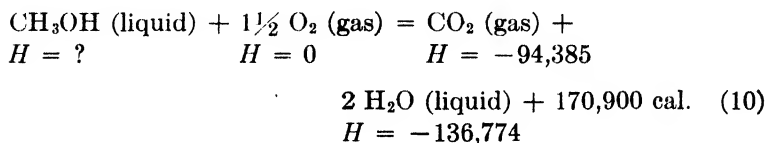
Heats of formation of many substances are to be found in tables. In the case of organic substances there are more likely to be found the heats of combustion. The chemist is supposed to be able to figure out the equation for the combustion. He knows that compounds of carbon, hydrogen, and oxygen are completely burned to carbon dioxide and (liquid) water. When the compound contains other elements he may have to obtain special information in order to write out the equation that is to be balanced.

For illustration of the method, let us find the heat of the formation of liquid methyl alcohol at constant pressure from carbon monoxide and hydrogen gases at 18° and 1 atm., the standard conditions adopted by "International Critical Tables." Most of their heat data are expressed in kilojoules, but the heats of combustion are given in kilogram-15°-calories. After converting heats in joules to heats in 15°-cal. by multiplication by the given conversion factor, 0.23895 (= 1/4.185), we have the following data for 15°-gram-calories (abbreviated to cal₁₅). Heats of formation per mole: for CO, 26,428; for H₂O (liquid), 68,387; for CO₂, 94,385; for the gaseous elements H₂ and O₂, zero. The heat of combustion of one mole of liquid methyl alcohol is 170,900, when the water formed is liquid.

The thermochemical equation will be



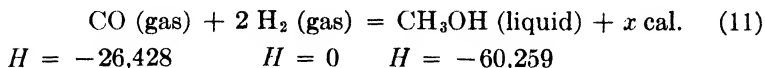
The equation for the combustion, with the heat contents written underneath, is



Notice that the heat content of two moles of water is twice that of one mole. The heat contents of the products sum up to -231,159. The quantity 170,900 is $-\Delta H = H_{\text{rea}} - H_{\text{pro}}$, and therefore

$$\begin{aligned} H_{\text{rea}} &= -\Delta H + H_{\text{pro}} = 170,900 - 231,159 = -60,259 \\ &= H \text{ for CH}_3\text{OH} \end{aligned}$$

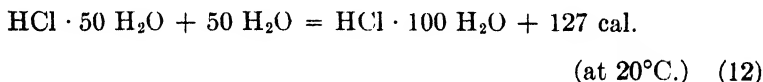
We now have all the heat contents involved in the reaction (9) and may write



During the reaction the heat content of the substances changes from $-26,428$ to $-60,259$. This is a decrease of $+33,831$ cal. $-\Delta H = x = 33,831$ cal.

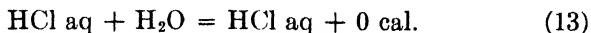
We have carefully distinguished in our equations the state of aggregation of each substance, because the heat content depends greatly upon it. Thus the heat content of a mole of any vapor very considerably exceeds that of a mole of the liquid at the same temperature and pressure, as heat must be added to convert the liquid into vapor.

The heat content of a gram of a solution depends on the composition as well as on the temperature and pressure. In thermochemical equations involving solutions the concentration must be noted. A very good way, and one much used, is to state the concentration in the form of a chemical formula, for example,



This in no way implies that $\text{HCl} \cdot 50 \text{H}_2\text{O}$ or $\text{HCl} \cdot 100 \text{H}_2\text{O}$ exists as a chemical compound.

When a sufficiently large quantity of water has been added to a solution, so that the solution is extremely dilute, the addition of another mole of water produces a negligible heat effect. Such a sufficiently large quantity of water is usually denoted by the symbol aq. Thus,



138. The Measurement of the Heat of Reaction.—We shall here consider the principle of one method. For the measurement of the heat of reaction the experiment is usually divided into two parts, both parts being either at the same constant pressure or at the same constant volume. In the first part, the experimenter determines the change of temperature produced as a result of the reaction, all gain or loss of heat being carefully

avoided (or the appropriate corrections being made). In the second part, the experimenter determines how much heat must be added or subtracted after the reaction in order to restore the initial temperature. An excellent way to do this is to heat the system with an electric heater immersed in the contents of the calorimeter and to measure the electrical energy dissipated in the heater. We say that this energy is quantitatively converted into heat, meaning that the heating effects might have been produced by adding a definite quantity of heat from a warmer body.

If the reaction is endothermic, the temperature falls from T_1 to T_2 , and we measure directly the electrical energy necessary to warm the system up to T_1 again. The electrical energy expended in warming up the heater itself should of course be subtracted, unless the heater was also present when the chemical reaction was carried out. The energy necessary to raise the temperature to its initial value is equal to the gain of energy or the gain of heat content attending the reaction at constant temperature, according as the experimenter is working at constant volume or at constant pressure.

If the reaction is exothermic, we first restore the system to its initial temperature in any convenient manner, and then measure the electrical energy necessary to produce the same rise of temperature of the calorimeter plus products as was produced in the chemical reaction. This quantity of energy is equal to the quantity we removed in bringing back the initial temperature, and is equal to the loss of energy or the loss of heat content attending the reaction.

If the heat capacities of the products are already known, then the experimenter can simply calculate the heat of reaction from the rise or fall of temperature as measured in the first part of the work. The heat capacity of the whole system, which we shall designate by C , equals the sum of the heat capacities of the various phases of the products plus the heat capacity of the calorimeter, which in turn is equal to the sum of the heat capacities of its various parts. The specific heats of these parts are known, and multiplication of these specific heats by the masses of the parts, and final addition of these products give the heat capacity of the calorimeter. The heat capacity of a solution

depends on the concentration, and must be known for the particular concentration and temperature.

Let the initial temperature be T_1 and the final temperature be T_2 . Then the product $C(T_2 - T_1)$ is the quantity of heat that must be added to change the temperature from T_1 to T_2 , and (whether it turns out positive or negative) is the heat of reaction at the initial temperature T_1 . The heat capacity C should really be an average value over the interval from T_1 to T_2 , provided this interval exceeds a few degrees. But the heat of reaction does not refer to the average temperature, but to the initial temperature, as has been emphasized throughout.¹

139. The Effect of Temperature and of Pressure on the Heat of Reaction.—We shall discuss here only reactions at constant pressure. When we know the heat of reaction $-\Delta H_1$ at one temperature T_1 we are in a position to calculate the heat $-\Delta H_2$ at another temperature T_2 by means of a very simple principle, provided that we can estimate the heat h_{rea} necessary to change the temperature of the reactants from T_1 to T_2 , and also the heat h_{pro} necessary to change the temperature of the products from T_1 to T_2 . The principle is this: the total increase of the heat content in changing the reactants at the temperature T_1 into products at the temperature T_2 would be the same, whether we first raise the temperature (increase of H is h_{rea}) and then let the reaction take place at T_2 (increase of H is ΔH_2), or whether we first conduct the reaction at T_1 (increase of H is ΔH_1) and then warm up the products to T_2 (increase of H is h_{pro}). Figure 42 illustrates these considerations. We have then the equation

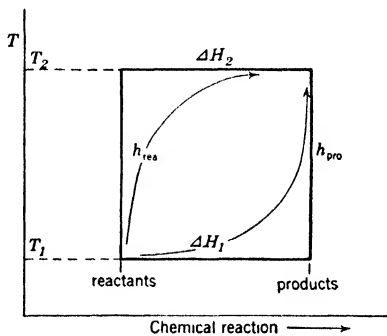


FIG. 42.—Calculation of the effect of temperature on the heat of reaction.

$$h_{\text{rea}} + \Delta H_2 = \Delta H_1 + h_{\text{pro}}. \quad (14)$$

¹ This was pointed out by the late Prof. Theodore W. Richards, who found that specialists had often erred in this respect. He noted further, that if we multiply $(T_2 - T_1)$ by the heat capacity of the *reactants*, we obtain the heat of reaction at T_2 . *J. Amer. Chem. Soc.*, **25**, 209 (1903).

If we can find from tables the specific heats at constant pressure of the reactants and the products, we can easily compute the heats h_{rea} and h_{pro} . Strictly speaking, we should use the average specific heats over the interval from T_1 to T_2 , but in practice the specific heats for either temperature may be used if the interval is not too great between them, as the specific heats do not vary with temperature too greatly. When the specific heats are substituted into Eq. (14) the result is usually known as Kirchhoff's law. A similar principle holds for calculating ΔE_2 from ΔE_1 and the constant volume specific heats.

A similar method may be applied for determining the effect of pressure on the heat of reaction, but this effect is so small that the method is not needed, even when gases are involved in the reaction.¹

140. The Heat Content Is Not the Quantity of Heat in a Substance.—In steam engineering problems, the engineer considers all addition or subtraction of heat to take place at constant pressure, and all pressure changes to occur without transfer of heat. Subject to these restrictions, the heat content may be taken as a measure of the quantity of heat in the steam² and is so considered. But chemists do not wish to abide by such restrictions, and dare not therefore think of the quantity of heat in a body. Strictly speaking, there is no such quantity. If there were, it would mean that the same quantity of heat would have to be added to produce a definite change of state, no matter how the change of state is produced, and this is proved to be wrong in all books on thermodynamics.³

The heat of reaction is not necessarily the same for a given change of state, unless throughout our operations we keep either

¹ The energy, the pV product, and hence the heat content of a mole of an ideal gas (for which $pV = RT$, T being thermodynamic temperature) depend only on the temperature, and only in very precise work is it necessary to consider the deviations of real gases from the simple theory of gases, or to consider the changes of energy or of heat content of liquids or solids when the pressure is changed at constant temperature.

² Pressure changes without transfer of heat occur without change of heat content.

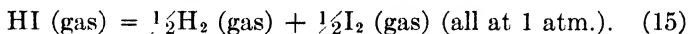
³ The proof depends on the facts that the energy change is determined by the initial and final states, but the work done is not, and therefore the heat effect cannot be so determined, but may vary according to the nature of the process.

the pressure or the volume constant. It is for this reason that we have introduced the energy and the so-called heat content into this chapter, instead of dealing in an ambiguous way with quantities of "heat."¹

141. The Effect of Temperature on Chemical Equilibrium.—

Suppose we have some substances in chemical equilibrium with respect to some chemical equation, at a definite temperature and pressure, and then change the temperature, obtaining a new condition of equilibrium, in which the concentrations or partial pressures or activities of the substances will in general be different from those obtaining at the original temperature. Such an equilibrium, which is "displaced" by changing the temperature,² has been called a "mobile equilibrium."

As an example, consider a gaseous mixture of hydrogen, iodine, and hydrogen iodide in chemical equilibrium at 500°C. with respect to the reaction



If the temperature be raised to 510° and equilibrium obtained again, there will be less HI and more I₂ and H₂ in the equilibrium mixture, that is, reaction (15) will have proceeded further from left to right.

This is connected with the fact that the reaction (15), read from left to right, is endothermic, heat being absorbed in the reaction at 500 or at 510°.

From thermodynamics and the simple theory of gases the following equation has been derived:

$$(d \ln K_p / dT) = \Delta H / RT^2, \quad (16)$$

where K_p is the equilibrium constant for the reaction in terms of partial pressures, and ΔH is the increase in heat content due to the reaction at the temperature T . The left-hand side of the equation represents the rate of increase in the natural

¹ Heat was at one time believed to be a substance, and the elementary teaching of topics on heat is still not in all cases free of the idea. When, at the beginning of this chapter, we spoke of the removal of a definite quantity of heat from the mixture of sulphuric acid and water, we were correct. It is exactly when heat is being transferred from one body to another, that we can measure it.

² Or by changing the pressure.

logarithm of the equilibrium constant with temperature. When products are formed to a greater extent at equilibrium on raising the temperature, K_p is also greater, since in writing the equilibrium constant the products are placed in the numerator, and the logarithm of K_p is greater when K_p is greater. Equation (16) shows therefore that when ΔH is positive (endothermic reaction) the equilibrium constant is increased at higher temperatures and hence the reaction goes further from left to right.

The quantity ΔH does not change greatly with temperature, and Eq. (16) can be easily integrated when ΔH is assumed constant, giving the equation

$$\ln K_p = -\Delta H/RT + \text{a constant}, \quad (17)$$

from which, if we know the value of ΔH , K_p may be calculated for a desired temperature when it is known at another temperature. According to Eq. (17) we should obtain a straight line if we plot $\ln K_p$ (or $\log K_p$) against $1/T$, and this is found to be the case. It is possible to improve Eq. (17) in various ways, but this is of interest only to specialists.

An exact equation, not dependent on the simple theory of gases or other simple theories, holds for any chemical reaction, whether gases, liquids, or solids, any or all, are involved in the reaction. This is given by Lewis and Randall:

$$(d \ln K_a/dT)_p = \Delta H/RT^2, \quad (18)$$

where K_a is the equilibrium constant in terms of activities and ΔH is the increase of heat content due to the chemical reaction when the reactants and products are all in their standard states. The pressure is supposed constant during the change of temperature, as signified by the subscript p . In the derivation of the equation it is assumed that the activity is taken as unity for each substance when at its standard pressure and not only at the temperature T , but also at other temperatures. The standard pressure is usually 1 atm. but may be chosen arbitrarily.

When the reaction takes place in a dilute solution, mole fractions or even concentrations may be used instead of activities in computing the equilibrium constant of Eq. (18).

142. The Effect of Pressure on Chemical Equilibrium.—In Chap. XX, under the heading Haber Equilibrium, it was

pointed out that, although the simple theory makes K_p , the equilibrium constant in terms of partial pressures, constant at constant temperature, and independent of variations of pressure, yet the amount of products formed at equilibrium may vary with the pressure. For a reaction among gases the simple theory gives

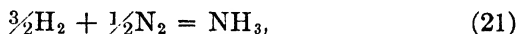
$$(d \ln K_p/dp)_T = 0 \quad (19)$$

for variations at constant temperature. It also gives the more informative equation

$$(d \ln K_x/dp)_T = -\Delta V/RT, \quad (20)$$

where K_x is the equilibrium constant in terms of mole fractions and $-\Delta V$ is the decrease of the volume of the gases as a consequence of the chemical reaction, at constant pressure and temperature, for which the equilibrium constant is written.

Thus, when there is a volume decrease at constant pressure, as in the reaction



K_x is greater at a higher pressure, and this means that the reaction goes further from left to right, since the products of the reaction are written in the numerator of the equilibrium constant.

When the chemical reaction does not cause formation or disappearance of gases the effect of pressure on the equilibrium is very slight.

143. Non-mathematical Treatment of the Displacement of Equilibrium.—Without the aid of equations we can predict the direction in which temperature and pressure will displace the equilibrium, if we know whether heat is absorbed or evolved and whether the volume increases or decreases in a displacement of the equilibrium, that is to say, when the reaction takes place to a certain extent, starting with a mixture not very different from the equilibrium mixture. The rules are simple and have been deduced thermodynamically without the aid of simplifying assumptions.

If, when we start with a mixture nearly at equilibrium and observe the heat effect produced when the reaction proceeds from left to right at constant temperature and pressure, we find that heat is absorbed, then the effect of an increase of temperature will be to displace the equilibrium in the same direction (from

left to right). But if heat is evolved under such conditions, the effect of temperature will be the opposite. The effect of temperature will be zero if heat is neither absorbed nor evolved under the conditions.

If, when we start with a mixture nearly at equilibrium and observe the volume change produced when the reaction proceeds from left to right at constant temperature and pressure, we find that the volume decreases, then the effect of an increase of pressure will be to displace the equilibrium in this same direction. Again, the effect of pressure is opposite if the volume increases, and is zero if the volume is unchanged.

These two rules are forms of LeChatelier's principle of mobile equilibrium. LeChatelier combined them into one rule, but this will not be given, as it is not so easy to comprehend it.

These two rules apply to the displacement of equilibrium. They do not apply to an explosive process, but after the explosion they will apply, if equilibrium is then reached with regard to the reaction and can be displaced by variations of temperature and pressure.

The necessity of considering a mixture nearly at equilibrium will be illustrated by considering the solubility of sodium hydroxide in water. When solid sodium hydroxide is treated with pure water, heat is evolved. We might hastily suppose that the solubility would decrease with rising temperature. But the fact is, that it is more soluble at 25 than at 20°, showing, by application of the rule, that when the solid dissolves in a nearly saturated solution, heat is absorbed. In this case, the solid that is in equilibrium with the saturated solution at these temperatures is not NaOH, but $\text{NaOH} \cdot \text{H}_2\text{O}$. But even when there is no such formation of a compound, we must be cautious. Above 65° the solubility also increases with rising temperature, and in this region of temperature the saturated solution is in equilibrium with anhydrous NaOH.

Book References

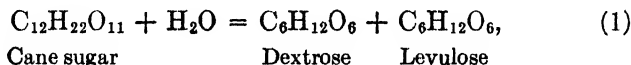
For further general information on the subjects discussed in this chapter, the reader is referred to MacDougall: "Thermodynamics and Chemistry," 2d ed., John Wiley & Sons, Inc., New York, 1926; and Lewis and Randall: "Thermodynamics," McGraw-Hill Book Company, Inc., New York, 1923. The most complete compilation of numerical data will be found in "International Critical Tables," Vol. 5, McGraw-Hill Book Company, Inc., New York, 1929.

CHAPTER XXVIII

THE VELOCITY OF CHEMICAL REACTIONS

Throughout the preceding chapters we have had a central thread of thought. We have been obliged temporarily to digress from time to time, in order to introduce facts or principles necessary for the discussion of equilibrium, and some of these topics are important in their own right, but our principal topic of discussion has always been equilibrium. The present chapter is no exception, for the velocity of a chemical reaction may be regarded as the velocity with which a system of chemical substances approaches a condition of equilibrium.¹

144. Definition of Velocity.—The velocity of a chemical reaction may be defined, after we have written the equation for the reaction, as the speed with which the concentration of some product increases, or that of some reactant decreases. Consider for instance the reaction



which takes place rather rapidly in water solution if a little strong acid is present. Let c_c be the number of moles of cane sugar per liter in the solution at any time t in minutes, and let c_d and c_l be the numbers of moles per liter of dextrose and levulose, respectively, at the same time. Then the reaction velocity V may be defined as

$$V = dc_d/dt \quad (2a)$$

or

$$V = dc_l/dt, \quad (2b)$$

where dc_d is the increase in the number of moles of dextrose per liter in the very brief time dt , and dc_l the equal increase in the

¹ Relative, of course, to some particular sort of chemical change (see Chap. I, Sec. 4).

number of moles per liter of levulose; or it may equally well be defined as

$$V = -dc_c/dt \quad (3a)$$

or

$$V = -dc_w/dt, \quad (3b)$$

where $-dc_c$ and $-dc_w$ are the decreases in the numbers of moles per liter of cane sugar and water, respectively. However, as the reaction is carried out in the presence of a large excess of water, it is not convenient in this case to define the velocity with respect to the concentration of water, as this is difficult to measure with accuracy. In this particular case the progress of the reaction can be followed by measuring the rotation of polarized light in a polarimeter.

In the reaction above, one molecule each of every substance occurs in the chemical reaction, and hence the velocity is the same with reference to each. But if two moles of a substance whose symbol is A react with one mole of B, it will make a difference which substance is used to define the reaction velocity, unless, as is sometimes done, we divide the concentration of A by 2, thus obtaining a sort of normality. The reaction velocity in terms of normality will be the same, whichever substance is used for the definition.

145. The Velocity Constant and the Order of Reaction.—

The velocity of the reaction at constant temperature will depend on the concentrations of the reactants. Suppose that the concentration of cane sugar is doubled without appreciably changing the concentration of water. This is easily managed if the original concentration of sugar is quite small. Then in a liter of solution there should be twice as many molecules of sugar in circumstances favorable for the reaction as there are before the doubling of concentration. Hence the number of molecules of sugar in the liter that react per minute ought to be doubled. In general, so long as the solution is dilute, the velocity of the reaction should be proportional to the concentration of the sugar. And, in so far as it may be practicable to change the concentration of the water, the number of opportunities for the reaction ought to be increased directly as the concentration of water is increased. When both concentrations

are variable, the velocity of the reaction will vary jointly with the concentration of cane sugar and the concentration of water, and therefore directly as the product of the two concentrations. In calculus notation,

$$V = -dc_c/dt = k_f c_c c_w. \quad (4)$$

Here the factor of proportionality is written k_f , the subscript being used to remind us that we are here considering the velocity of the *forward* reaction, that is, reaction (1) proceeding from left to right as written. k_f is called the velocity constant. Its value depends on the temperature and on the catalytic effect of any foreign substances that happen to be present, but it is independent of the concentrations of the reactants, provided that the differential equation (4) is correct.

If definite quantities of sugar and water are treated with a definite small quantity of a strong acid, reaction (1) proceeds. The concentration of the mineral acid is of importance, indeed, the velocity constant k is proportional to the hydrogen-ion activity of the solution, but the acid is not used up during the experiment, and Eq. (4) needs no correction. As the reaction proceeds, the concentration of sugar decreases progressively toward zero. The concentration of water cannot change much, if we have started with a reasonably dilute solution. According to Eq. (4) the reaction velocity will therefore progressively decrease, approaching zero velocity as the sugar nears exhaustion. This variation of velocity during any given experiment is what necessitates the application of the calculus.

If the concentration of sugar is experimentally determined at various values of the time, and is plotted (c_c) against the corresponding time (t), a curve like Fig. 43 is obtained. The velocity V at the point given by the time t_1 and corresponding concentration c_1 is the ratio of the dotted lines $-dc$ and dt . The oblique broken line is tangent to the curve at the point t_1, c_1 .

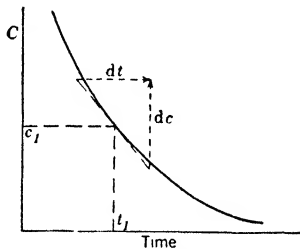


FIG. 43.—Illustrating the velocity of a chemical reaction.

We can proceed to determine such a curve experimentally and then test the applicability of Eq. (4) by drawing tangents and the lines $-dc$ and dt , computing V and finding out whether k_f , calculated as $V/c_c c_w$, is really the same at different times, as theory predicts.

A more elegant method is to integrate the differential equation (4), thus obtaining the equation of the curve. If we assume c_w constant, and write k for the constant product $k_f c_w$, the result of integration is

$$\ln c_c = -kt + \text{a constant of integration.} \quad (5)$$

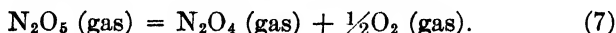
The constant of integration depends on what the concentration of sugar was at the time when $t = 0$. Putting $t = 0$ in Eq. (5), we find that the constant of integration equals the natural logarithm of the initial concentration, which we may denote by c_0 . Then we have

$$\ln c_c = -kt + \ln c_0. \quad (6)$$

By means of Eq. (6) the constant k can be computed for the various times of observation and examined for constancy.

A reaction such as (1) involves two reacting molecules and is called a bimolecular reaction, or a reaction of the second order. In dilute solutions it behaves, however, like a reaction of the first order and follows Eqs. (5) and (6), k being in fact constant. Equations (5) and (6) are for a reaction of the first order, in which only one molecule occurs on the left-hand side of the chemical equation.

Chemical reactions truly of the first order have proved to be very rare. An example of a reaction believed to be of the first order is the decomposition of nitrogen pentoxide:



Many reactions formerly supposed to be of the first order, because Eq. (6) is satisfied better than the equations developed for reactions of higher order, are known to involve more than one reactant molecule, even though only one such occurs in the chemical equation as ordinarily written. The biologist should therefore guard against the supposition that a chemical reaction of the first order is involved, simply on the ground that an equation of the form of Eq. (6) applies to his data.

The velocity of any complicated process is limited by the velocity of the slowest element of the process. If the velocity is limited by the slow process of diffusion, as is often the case, Eq. (6) is likely to be satisfied, quite independently of the true order of the reaction.

Equation (6) is convenient when we wish to refer to the concentration of the reactant left at any time t . When we wish to refer rather to the concentration of a product produced at any time t we may use the following equation:

$$\ln (A - c) = -kt + \ln A, \quad (8)$$

where A is the concentration of the reactant at the time when t is zero, and c is the concentration of a product at the time t , both concentrations being on the normality basis. This equation is readily derived from Eq. (6), if we note that $A - c$ is the concentration of the reactant left at any time t .

143. General Expression for the Mass Action Law for Velocity.

The law, that the velocity of a reaction is proportional to the concentration of each reactant, is called the mass action law for the velocity of reaction. Like the mass action law for equilibrium, it is most exact in dilute solution, and in the case of electrolytes, is to be applied to the individual ions, rather than to the whole electrolyte.

Consider the case where more than one molecule of the same substance is involved in the reaction, as in the gaseous reaction



There are two molecules of hydrogen iodide involved, and as the law makes the velocity proportional jointly to both of two concentrations, when they are different, it makes it proportional to the square of the concentration of the reactant, when the two reacting molecules are of the same kind. The differential equation is

$$-dc/dt = kc^2, \quad (10)$$

where c is the concentration of hydrogen iodide at any time t . In writing the velocity equation, each concentration is raised to the x th power, where x is the number of molecules of reactant occurring in the chemical equation.

147. Velocity and Equilibrium Constants.—Velocity studies of the forward reaction are most easily made when the forward reaction is almost quantitative, that is, goes practically to completion. When the reverse reaction can also occur to a measurable extent, the velocity of the forward reaction can still easily be studied in its early stages, before the concentrations of the products become important.

When a reaction that is practically reversible approaches equilibrium, an experimental measurement of the increase of concentration of a product gives us the *net* change, including the increase of products due to the forward reaction and the decrease of products due to the reverse reaction. At equilibrium, we say that forward and reverse reactions are both taking place, but at equal rates,¹ so that the amount of product formed per minute equals the amount destroyed in the reverse reaction.

Applying this idea, we obtain at once the mass action law for equilibrium from the mass action law for velocity. Thus for reaction (9), we have for the destruction of hydrogen iodide the equation

$$-dc_{\text{HI}}/dt = k_f c_{\text{H}_2}^2 \quad (11)$$

and for the formation of hydrogen iodide the equation

$$dc_{\text{HI}}/dt = k_r c_{\text{H}_2} c_{\text{I}_2}. \quad (12)$$

Equating the velocity of destruction to that of formation we obtain the result

$$k_r c_{\text{H}_2} c_{\text{I}_2} = k_f c_{\text{HI}}^2 \quad (13)$$

or

$$\frac{c_{\text{H}_2} c_{\text{I}_2}}{c_{\text{HI}}^2} = \frac{k_f}{k_r}. \quad (14)$$

The expression on the left-hand side of Eq. (14) is the mass action equilibrium constant in terms of concentrations. Denoting this by K_c , we have

$$K_c = k_f/k_r. \quad (15)$$

From the similarity in the rules for writing the mass action velocity constants and the mass action equilibrium constant

¹ Computed, when necessary, on the normality basis (Sec. 144).

it can be seen that Eq. (15) will apply, whatever the equation may be for the chemical reaction. The equilibrium constant equals the velocity constant for the forward reaction divided by that for the reverse reaction.

Since we know that the equilibrium constant, when we use concentrations in it instead of activities, is not truly constant, except for very dilute solutions, it is clear that the mass action velocity constants cannot be truly constant, using concentrations, except again for very dilute solutions. No general principles enable us to state that the law for velocity is accurate in terms of activities.

148. Temperature and Reaction Velocity.—The velocity of a chemical reaction increases as a rule two- or threefold when the temperature is raised $10^{\circ}\text{C}.$, other conditions being constant. Let k_T be the velocity constant at T° and k_{T+10} be the velocity constant at $T + 10^{\circ}$; and let the ratio of the constants be Q_{10} :

$$Q_{10} = k_{T+10}/k_T. \quad (16)$$

The ratio Q_{10} has a value from 2 to 3 for most chemical reactions and is approximately constant as we change the temperature. A more nearly exact equation for the variation of the velocity constant k with temperature is

$$\ln k = E/RT + J, \quad (17)$$

where J is a constant and E is another constant called the critical energy. This equation resembles in form Eq. (17) of the previous chapter. The critical energy is not to be confused with the energy of the reactants. In statistical theories of reaction rate it has to do with the energy assumed to be necessary to add to a normal molecule in order to activate it, putting it in a special condition favorable to chemical action.

The effect of a 10° rise of temperature on the velocity of a purely physical process, such as diffusion, is usually to multiply the velocity by more than 1 but less than 2. By a determination of the effect of temperature on the speed of a biological process it has sometimes been possible to decide whether the speed of the process is conditioned by a chemical or a physical process. Thus, the effect of temperature on the speed of conduction of a

signal through a nerve is large, indicating that nerve conduction involves a chemical process.

A large body of data on velocity constants and the influence of temperature will be found for chemical and biochemical reactions in "International Critical Tables."¹

149. Catalysis.—A catalyst for a reaction may be defined as any material, other than a substance which appears in the chemical equation as a reactant, that increases the velocity of the reaction when added to the reactants or brought into contact with them. Sometimes a product of the reaction is catalytic: the reaction is then classified as autocatalytic. An anti-catalyst decreases the velocity of the reaction, without acting as a product to speed up the reverse reaction or destroying the reactants. If we write the differential equation for the velocity, we may then define a catalyst as a material that increases the velocity constant, an anti-catalyst as one that decreases it.

In many cases the effect on the velocity constant is proportional within reasonable limits to the concentration of the catalyst. This is the case with the catalysis by hydrogen ion of the inversion of cane sugar, and this fact has been made the basis of a method for determining hydrogen-ion concentration. This method cannot however compare in convenience or excellence with the usual methods for the determination of pH.

Some definitions of catalyst require that the material undergo no change of state, but common usage does not always adhere to this limitation.

When the catalyst does not undergo any change of state, it cannot by its presence affect an equilibrium mixture to displace the equilibrium. Otherwise, by alternately adding and removing the catalyst, which would on the average require no work, it would be possible to make a chemical reaction go back and forth repeatedly. This would, however, be impossible, as by ingenious devices we could get work out of the system for nothing, or at the expense of the heat of the surroundings, both of which are excluded by the two laws of thermodynamics.

We dare assert that at equilibrium the forward and reverse reactions are still going on, but at equal rates. Since the catalyst does not disturb the equilibrium, it must affect both velocities

¹ Vol. 7, 1930.

to an equal extent. It is in fact found that a catalyst for the decomposition of ammonia into its elements is also a catalyst for its formation. The effectiveness of the catalyst may be influenced by the composition of the fluid in contact with it. Hence an excellent catalyst for a forward reaction in its early stages might be a poor one for the reverse reaction in its early stages, but at equilibrium the catalyst must be equally good for forward and reverse reactions, provided it undergoes no change of state.

Sometimes it may be possible for a system to go from a state *A* either to a state *B* or to a state *C*. One catalyst may bring about equilibrium with respect to the change *A* to *B*, and a different one may bring about equilibrium with respect to the change *A* to *C*. If now the change *B* to *C* or *C* to *B* does not readily occur, then the choice of catalyst will determine whether the products *B* or the products *C* are formed.

For the synthesis of ammonia pure iron is a good catalyst (at temperatures above 500°C.). It is improved by adding small quantities of other metals or their oxides, which are called promoters.

In many cases, as in the synthesis of ammonia, the catalytic agent is not soluble in the phase or phases in which the reactants occur, and the catalytic action appears to depend in large measure on the adsorption of reactants on the surface of the catalyst. There is an advantage, if the products are not strongly adsorbed.

Further general information must be sought in special treatises on catalysis and in the larger texts on physical chemistry.

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